FINAL REPORT -PHOTOASSISTED ELECTRON TRANSFER REACTIONS OF APPLICATION TO MINE WASTEWATER CLEANUP: METAL-COMPLEXED CYANIDES

MINE WASTE TECHNOLOGY PROGRAM ACTIVITY IV, PROJECT 3A

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Foreward

Industries are attempting to develop and modify their existing operations to manufacture products with environmentally-safe technologies. Wastes generated by these industries are often unsightly and can threaten public health as well as degrade the environment, especially if they are left untreated or are improperly treated. Mine wastes are particularly suspect because of the presence of Amobile toxic constituents@ such as, for examples, cyanide that remains in tailings ponds and heap leach pads or acid mine drainage that contains heavy metals leached from sulfide minerals in exposed ore bodies.

The U.S. Environmental Protection Agency (U.S. EPA) is charged by Congress with protecting the nation=s land, air, and water resources. Under mandate of national environmental laws, the U.S. EPA strives to formulate and implement actions leading to a balance between human activities and nature=s ability to support and nuture life. Such laws direct the U.S. EPA to define environmental problems and thereby perform research, measure impacts, and find solutions. In this regard, the U.S. EPA=s National Risk Management Research Laboratory (NRMRL) is responsible for planning, implementing, and managing research, development and demonstration programs to provide an authoritative and defensible engineering basis in support of the U.S. EPA=s policies, programs and regulations with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities.

Similar responsibilities have also been assigned to the U.S. Deparment of Energy (U.S. DOE) through the Pittsburg Energy Technology Center (PETC), one of several U.S. DOE centers in charge of planning, implementing, and managing research and development programs. In June 1991, an Interagency Agreement was signed between U.S. EPA and U.S. DOE , IAG No. DW89935117-01-0, which made funds available to support the Western Environmental Technology Office (WETO) and their operating contractor, MSE Technology Applications, Inc. (MSE-TA), as well as Montana Tech of The University of Montana (Montana Tech) for the development of the Mine Waste Technology Program (MWTP).

The MWTP serves as a telecommunication and technology transfer center for the training and education of students (kindergarten through college) and professionals (K-12 teachers through mining representatives), a communication link that is vital to the general public=s undertsanding of the issues surrounding mine wastes and mining-related activities. Also, the MWTP funds projects for researchers to develop, demonstrate and/or implement technologies that solve environmental problems related to mine wastes and mining-related activities. Written reports of the projects are used to inform the user and professional communities and simultaneously complement the technology transfer facet of the MWTP. In this regard, workplans, quality assurance project plans (QAPP), and final reports on quality assurance/quality control (QA/QC) data are standard communications of the MWTP. The ensuing manuscript is a final report for presenting the QA/QC data that was obtained for MWTP Activity IV, Project 3A, APhotoassisted Electron Transfer Reactions of Application to Mine Wastewater Cleanup: Metal-Complexed Cyanides.@ Project objectives were to identify and evaluate appropriate

technologies for using ultraviolet radiation to remediate waters containing metal-complexed cyanide via photooxidation and then to recommend whether follow-up research was needed or not.

Executive Summary

This final report presents QA/QC data obtained for MWTP Activity IV, Project 3A, APhotoassisted Electron Transfer Reactions of Application to Mine Wastewater Cleanup: Metal-Complexed Cyanides.@ Several photoassisted electron transfer reactions were explored for the cleanup of this mobile toxic constituent commonly found in mine wastewaters. Each of these reactions involved electron transfer with a solid photocatalyst and a dissolved photosensitizer, which, in this study, were limited to anatase (titanium dioxide, TiO_2) and hydrogen peroxide (H_2O_2), respectively. These same reagents were successfully used and demonstrated by Young (1996) for free cyanide (CN^-) in MWTP Activity IV, Project 3 (Ref. 1).

Because metal-complexed cyanides contain cyanide which is in a reduced state, only photooxidation experiments were conducted in an effort to oxidize the cyanide to less or non-hazardous substances, nitrite and nitrate. However, the strength of the metal-cyanide bond is dependent on the type of metal; weak-acid disociables (WADs) refers to metals which disociate under moderate acid conditions (approximately pH 3.5 to 7) and strong-acid disociables (SADs) refers to metals which disociate, if at all, at lower pH values. In this regard, a suite of metals were examined and are listed in increasing order of metal-cyanide bond strength: $Zn(CN)_4^{2-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Au(CN)_2^-$, and $Co(CN)_6^{4-}$. The Zn-complex represents one of the weakest WADs and the Co-complex represents one of the strongest SADs. Reaction efficiencies were determined and compared for all experiments. Experiments were conducted in the absence and presence of UV-radiation.

Results show that photo-oxidation of metal-complexed cyanides works but, under the conditions examined, its efficiency is dependent on the photolytic process as well as the metal type. Results indicated that hydrogen peroxide will oxidize all the complexes in the absence of UV (i.e., Degussa Process). However, when the UV source was on, all were observed to be remediated even further. As expected, anatase showed no response in the absence of UV but worked well in its presence. Under the conditions examined, hydrogen peroxide worked better. The lack of 100% remediation at all times is believed to be the result of not allowing enough time and/or not having enough reagent for the reaction to occur completely. For UV-irradiated anatase, other reasons could involve surface passivation due to the formation of precipitates as well as a lack of adsorption due to surface bonding (an attractive force) being weaker than coulombic interactions (a repelling force under the experimental pH conditions that were used). Because of the different results between hydrogen peroxide and anatase, a new mechanism was proposed in which UV-irradiated anatase forms holes (h^+) to react with the metal-complexed cyanides. Although these technologies are effective, they are relatively slow (at least under the conditions examined). Consequently, future studies are recommended to enhance the reaction rates via numerous methods. Lastly, due to difficulties in measuring the concentrations of some metal-complexed cyanides, it is recommended that a different technique be adopted and used. In this regard, a strategy is believed to have been developed for this.

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1. INTRODUCTION

This final report was prepared from technical information and validated Quality Assurance/Quality Control (QA/QC) results obtained by ACZ Laboratories, Inc. in Steamboat Springs, Colorado, from samples treated experimentally at Montana Tech of The University of Montana (Montana Tech) in Butte, Montana, for the Mine Waste Technology Program (MWTP), Activity IV, Project 3 - APhotoassisted Electron Transfer Reactions of Application to Mine Wastewater Cleanup: Metal-Complexed Cyanides.@ All enclosed materials are follow-up to the approved MWTP Activity IV, Project 3A, Work Plan and Quality Assurance Project Plan (QAPP) dated June 1995 and October 1996, respectively (Ref. 2-3). The information and results are described in accordance with the requirements of the Interagency Agreement (IAG) Activity IV Scope of Work which was signed in June 1991 by the U.S. Environmental Protection Agency (U.S. EPA) and the U.S. Department of Energy (U.S. DOE) to initiate work on the MWTP. Furthermore, this MWTP final report addresses the testing and evaluation of a promising photolytic technologies for the remediation of mobile toxic constituents in mine wastewaters identified in MWTP Activity I Prioritization Reports (Ref. 4-8), metal-complexed cyanide.

1.1   Relevance to MWTP

Discharge waters from various municipal and industrial operations transport many dissolved chemicals that have adverse effects on the environment of both plant and animal life. For example, dissolved chemicals may leach various heavy metals which would otherwise remain immobile. Aquatic life of all sorts become sick or die due to the toxicity of both the dissolved chemicals and metals. Many wastewater processing technologies that are currently available or being developed emphasize the removal of the dissolved chemicals and the heavy metals as cations. The anions associated with metal cations can be equally as toxic but are largely ignored. In this regard, cyanide (CN^-) and some of its metal complexes have been recognized as being toxic. Their remediation has been considered paramount at several locations in Montana and throughout the United States (Ref. 4-8).

Impetus for this study emanated from the previous and successful study on free cyanide (Ref. 1) and from technical concerns regarding the effectiveness of non-photolytic cyanide-kill processes that have been raised due to the lack of information on the fate of cyanide species and their reaction kinetics and products (Ref. 5,9). Further impetus comes from concerns of citizens near sites contaminated with cyanide such as Chicago Mining Company's heap leach operation, Pony, Montana, where residents detected cyanide in their well waters. Similar problems have been noted for other sites in Montana and throughout the United States (Ref. 4-8). In summary, photolytic technologies have been examined and are discussed in this final report for remediating metal-complexed cyanide.

Cyanide can be found in solutions as free cyanide, as weak complexes with metals such as cadmium, zinc and copper, and as strong complexes with other metals including iron, cobalt, mercury, silver, platinum, palladium and gold (Ref. 10). If cyanide is allowed to enter natural waters, it may be ingested by animals and subsequently absorbed by their gastrointestinal and respiratory tracts. The mean lethal

dose to the human adult is 50 to 200 mg (Ref. 9). Huiatt et al. (Ref. 9), Wheatington (Ref. 11), and Young et al. (Ref. 12,13) investigated numerous cyanide treatment technologies using information from literature, industrial, and government sources and noted that oxidation technologies were the only methods which destroyed metal-complexed cyanides. The other technologies, a mix of physical, adsorption and complexation methods, produced a concentrated waste which required further treatment. Oxidation methods included biological destruction, chemical addition, and photolysis. Biological destruction is only used industrially at the Homestake Mine in Lead, South Dakota (Ref. 14,15) but research is ongoing at other sites (Ref. 16-21). Numerous sites throughout the world use oxidizing chemicals such as hydrogen peroxide, H_2O_2 (Ref. 22-25); Caro's acid, H_2SO_5 (Ref. 26-28); sulfur dioxide SO_2 (Ref. 29-32); and hypochlorite, OCl^- (Ref. 33-36) to destroy the complexes. Because these oxidative methods were criticized for being unable to treat strong metal complexes, Wheathington (Ref. 11) and Young et al. (Ref. 12,13) concluded that photolysis could be the most promising method for complete cyanide destruction with the most popular being UV-assisted hydrogen peroxide (Ref. 37-40) or titanium dioxide (Ref. 38-54).

1.2   Research Objectives

From the above discussions, it is clear that metal-complexed cyanide can be remediated by photolysis. Consequently, one aim of this project was to examine the effectiveness of photoassisted remediation of this mobile toxic constituent. Because nitrogen in cyanide is in a reduced state of -III, its remediation can only be accomplished by oxidation. Although cyanide and metal-complexed cyanide photolytic studies have been reported, especially with solid (i.e., heterogeneous) photocatalysts (Ref. 38-54), there appears to be very little published work with dissolved (i.e., homogeneous) photosensitizers (Ref. 37-39). After identifying the appropriate photolytic technology(ies) which could be used for remediation, a second goal of the project was to evaluate the most appropriate technology(ies) by determining reaction efficiencies. Ultimately, it was hoped that the appropriate technology(ies) would be developed for transfer to the sites where metal-complexed cyanide contamination is known to occur. As a final objective, the appropriate technology(ies) would be recommended for further study(ies).

2. PHOTOCHEMISTRY

2.1 Technology Background

Remediation research of polluted waters originating from active or inactive mine sites and associated materials handling procedures has primarily focused on bringing to the affected areas foreign substances and processes which could ultimately disturb a naturally established ecosystem. Remediation methods by, for example, lime addition are inherently expensive and make the sites difficult to revegetate. Overwhelming evidence shows that natural processes occur that heal environmental scars caused by mining activities. These processes include electron transfer reactions which lower the concentrations of "mobile toxic constituents" in surface and ground waters via interactions with electromagnetic radiation from the sun, ultraviolet (UV) radiation in particular. However, these naturally photoassisted processes suffer at night, on cloudy days, and in winter months. During these periods, artificial UV sources are needed to sustain the processes. Furthermore, because the processes may still proceed too slowly, photocatalysts or photosensitizers can be supplemented to absorb and transfer the UV radiant energy to the reactants thereby remediating the water within more acceptable time frames. Photocatalysts are predominantly solid semiconductors and photosensitizers are usually dissolved in solution.

In photolysis, solutions (or other sample types) are irradiated with electromagnetic radiation, usually UV, to promote electron transfer reactions between toxins (i.e., metal-complexed cyanide) and other available species. The toxins either undergo photoreduction or photooxidation to yield less toxic or non-toxic compounds depending on the reduction/oxidation (redox) chemistry of the system. Photolysis can be accomplished with direct or indirect techniques. Direct photolysis requires the substance being remediated to absorb the radiation. Indirect processes can be induced by having a second material absorb the radiation and then transfer the photo-energy to the substance being remediated. In this regard, solid semiconductors can be used such that they participate only as catalysts (heterogeneous photocatalysis). On the other hand, dissolved photosensitizers can either be consumed during the reaction (homogeneous photolysis) or participate as catalysts (homogeneous photocatalysis). These photoassisted processes are discussed below but, for simplicity, only as solid photocatalysis and dissolved photolysis.

2.1.1 Solid Photocatalysis

To date, most work has entailed studying the oxidation of toxic organic compounds using solid semiconductors as electron transfer photocatalysts to ultimately produce both carbon dioxide and water (Ref. 54-66). However, current emphasis appears to be on applying this successful technology to the oxidation of inorganic compounds in order to satisfy new and more stringent environmental regulations. Numerous solid photocatalysts have been reported to work well: TiO_2, ZnO, WO_3, CdS, SiC, Fe_2O_3 and certain zeolites (Ref. 54-57), to name a few. The anatase polymorph of TiO_2 has been preferred because of its cheap cost, relative abundance, and high quantum efficiency in converting photon energy into chemical energy (Ref. 48,50).

In order for these solid semiconductors to function as electron transfer photocatalysts, their band gap

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energies must be less than the absorbed UV radiation as determined from the equation:

$$E = h\nu \qquad\qquad [1]$$

where h is Planck's constant and ν is the frequency of the UV radiation. Upon absorbance, an electron is excited into the conduction band from the valence band where a "hole" is created (see Figure 2.1):

$$\text{semiconductor} \xrightarrow{h\nu} (e^- \, h^+) \qquad\qquad [2]$$
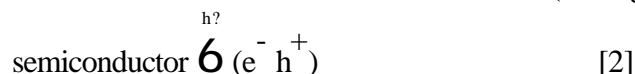
Because the band gap between the conduction and valence band edges lacks energy levels, the excited electron will reside at the conduction band edge whereas the hole will reside at the valence band edge. Consequently, the electron-hole $(e^- \, h^+)$ pair will be relatively stable possessing a lifetime that is long enough for electron transfer reactions to occur:

$$h^+ + D \rightarrow D^+ \qquad\qquad [3]$$

$$e^- + A \rightarrow A^- \qquad\qquad [4]$$

Clearly, electron donors (D) become oxidized when the release electrons to fill the holes (Reaction 3) and electron acceptors (A) are reduced when the consume the excited electrons (Reaction 4).

Solid electron transfer photocatalysis can not occur unless both A and D are preadsorbed at the semiconductor surface and the products, D^+ and A^-, do not react with respective excited electrons and holes to reproduce the reactants. Otherwise no net reaction results. Furthermore, the Nernst potentials of Reactions 3 and 4 must be thermodynamically favorable. Each of these requirements can be met by (1) using semiconductors that are amenable to the adsorption of both A and D but not A^- and D^+, (2) choosing a semiconductor whose band gap is appropriate for the electron transfer reactions to occur, (3) choosing ligands which react with the radical products to form inert species, (4) selecting appropriate pH conditions, (5) stirring/bubbling the system to remove the radical products from the surface, (6) depositing metals (i.e., platinum) at the surface as a co-catalyst to localize the excited electrons, and (7) promoting reactions between the radical products themselves. Clearly, the surface, electro-, solution, and analytical chemistries of the solid electron transfer photocatalytic reactions must be well understood before they can be induced and/or enhanced.

As already stated, solid photocatalysis has primarily been used to examine the oxidation of toxic organic compounds (Ref. 54-66); however, the oxidation of inorganic compounds is currently receiving much attention (Ref. 47-54). In addition, it is important to further note that the photoreduction of both organic and inorganic compounds is possible (Ref. 39,40,54-57,62) but is less frequently observed presumably because the reducing power of the excited electron is significantly lower than the oxidizing power of the hole and because the compounds must kinetically compete with oxygen and/or water as the electron acceptor (Ref. 62).

2.1.2 Dissolved Photolysis

Photochemical reactions in the absence of solid semiconductors have involved both organic and inorganic compounds and have been classified as either direct or indirect processes. In direct photochemical processes, the compound (designated as X in subsequent equations) absorbs the electromagnetic radiation to form an excited state which then reacts to form a variety of products (see Figure 2.2):

$$X + h\nu \rightarrow X^* \rightarrow products \qquad [5]$$

For most organic compounds, this reaction is typical of decompositions. For certain inorganic compounds, this reaction either (1) yields changes in oxidation states or (2) tranfers the photo-energy to water yielding hydroxyl radicals (OH^*) which can then decompose various organic compounds or react with other inorganic species to produce specific radicals (Ref. 38, 54-58). With indirect photochemical processes, photosensitizers absorb the radiation

$$S + h\nu \rightarrow S^* \qquad [6]$$

and then transfer the photo-energy to the compound thereby catalyzing the following reaction:

$$S^* + X \rightarrow S + X^* \rightarrow S + products \qquad [7]$$

or transfer the energy to another species (usually oxygen) to induce the following reactions:

$$S^* + O_2 \rightarrow O_2^* + S \rightarrow products + S \qquad [8]$$
$$O_2^* + X \rightarrow products \qquad [9]$$
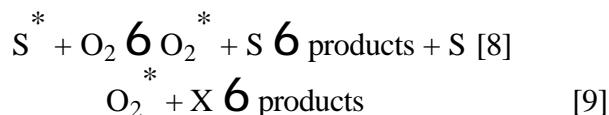
where the oxygen radical may participate as either a reactant or a co-catalyst. In some cases, the photosensitizer (S) is consumed in the process and is therefore not considered to be a dissolved photocatalyst.

Each of the radicals mentioned above (i.e., inorganic, organic, hydroxyl, specific, photosensitizer, and oxygen) are dissolved photocatalysts and can induce oxidation (electron donating) or reduction (electron accepting) reactions in the same manner as solid photocatalysts. However, the dissolved photocatalysts are not dependent on adsorption and other surface area phenomenon and, by comparison, can therefore be expected to enhance reaction rates by orders of magnitude, dependent only on the concentration of the dissolved photocatalyst. Other dissolved photocatalysts include photon-active redox couples where the oxidant would be the electron donor and the reductant would be the electron acceptor.

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2.2 E_H-pH Diagrams

Because photolysis involves electron transfer reactions, it is helpful to examine thermodynamic equilibrium diagrams such as E_H-pH diagrams to see what possible reactions may occur between reacting species and to see what products my be formed as the reaction occurs. In this regard, E_H-pH diagrams were generated using STABCAL (Ref. 67,68) and shown to be very reliable in previous and other ongoing MWTP projects (Ref. 1,69,70). STABCAL is a program developed for IBM-compatible personal computers to calculate various types of thermodynamic stability diagrams. In order to construct the diagrams for metal-complexed cyanides, thermodynamic data at 298K was predominantly obtained from NBS tables using a reference library within the STABCAL program [Ref. 71].

2.2.1 Cyanide

An E_H-pH diagram for cyanide at $1x10^{-3}$ M and 298K is illustrated in Figure 2.3. Cyanide is depicted to be predominantly stable at pH values greater than 9.23 and at E_H values just below the stability of water. In this regard water should directly oxidize cyanide to form cyanate (OCN^-):

$$CN^- + H_2O = OCN^- + 2H^+ + 2e^-$$ [10]

However, the reaction is slow because a large activation energy must first be overcome (Ref. 9). In this regard, it is important to note that photolysis can help overcome this energy barrier. The liberation of hydrogen cations (H^+) as depicted in Reaction 10 substantiates the precaution that pH-control is necessary to avoid toxic hydrogen cyanide gas formation and evolution. The E_H-pH diagram further predicts that continued oxidation should yield various nitrite (NO_2^-) and carbonate (CO_3^{2-}) species and eventually produce nitrate (NO_3^-):

$$OCN^- + 4H_2O = NO_2^- + CO_3^{2-} + 8H^+ + 6e^-$$ [11]
$$NO_2^- + H_2O = NO_3^- + 2H^+ + 2e^-$$ [12]

However, Reactions 11 and 12 are also hindered by slow reaction rates even in the presence of aerated or oxygenated solutions (Ref. 9). Previous investigations (Ref. 73,74) constructed E_H-pH diagrams for various metal/cyanide water systems but did not consider nitrites, nitrates, and carbonates as oxidation products. In this regard, this study marked only the second time that such species were considered as reaction products for incorporation into cyanide E_H-pH diagrams; the first was considered for MWTP Activity IV Project 3 (Ref. 1).

2.2.2 Metal-Complexed Cyanides

Figures 2.4-2.7 depict E_H-pH diagrams for the metal-cyanide complexes of interest, $Zn(CN)_4^{2-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{4-}$ and $Au(CN)_2^-$, at $1x10^{-3}$ M and 298K under metastable conditions such that the formation of cyanate, nitrite and nitrate was not allowed. Consequently, only the metals are shown to have a change in oxidation state. This can be expected for non-equilibrium conditions in

which the high activation energy barrier between cyanide and water prevents their reaction (see Reaction 10). Furthermore, as discussed above, this can also be expected of non-photolytic conditions.

These E_H-pH diagrams show that $Zn(CN)_4^{2-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{4-}$ and $Au(CN)_2^-$ are not thermodynamically stable at pH values below 7.2, 3.7, 3.2, 0.2 and <0, respectively. In this regard, it is clear that the complexes are listed in approximate order of increasing cyanide bond strength with $Zn(CN)_4^{2-}$ being the weakest (i.e., WAD) and $Au(CN)_2^-$ being the strongest (i.e., SAD). Furthermore, the stronger the complex, the larger the stability region it covers on the diagram. Surprisingly, since cobalt cyanide is reported to be the most refractory of these metal-cyanide complexes, it was not found to be the strongest thermodynamically. This may be the result of using free energy data determined from equilibrium constants obtained from an IUPAC CD-ROM computer library (see Appendix A and Ref. 75-82) as opposed to the NBS Tables used for the other complexes. In this regard, it is important to note that thermodyanamic data should come from one source as much as possible to avoid making suspect comparisons which may be the case here. Nevertheless, this report marks the first time in the literature that thermodynamic data was determined and depicted in an E_H-pH diagram for the cobalt-cyanide system.

Figures 2.8-2.11 depict E_H-pH diagrams for the same metal-cyanide complexes at 1×10^{-3} M and 298K but under stable conditions in which cyanate, nitrite and nitrate are allowed to form. Consequently, both the metals and cyanide are shown to change in oxidation state. This can be expected for equilibrium conditions in which the high activation energy barrier between cyanide and water is overcome perhaps upon exposure to UV radiation. In this regard, the band gap of anatase was superimposed on the diagram (see Figure 2.3).

Clearly, the metal-cyanide complexes are no longer found to predominate under wide-ranging E_H and pH conditions. In fact, the stability regions are below that of water and, in the case of gold cyanide, is non-existant. Oxidation reactions of the metal-cyanide complexes to yield cyanate are therefore expected:

$$M(CN)_x^{y-x} + xH_2O = xOCN^- + 2xH^+ + M^{y+} + 4ye^- \qquad [13]$$
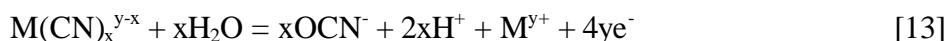
Depending on the E_H and pH conditions, the cyanate could continue to oxidize to nitrite and nitrate according to reactions 11 and 12 and the metal cation could precipitate as a pure metal, hydroxide, or oxide.

2.2.3 Anatase

Reactivities for electron-hole pairs produced at anatase (TiO_2) surfaces were superimposed on the stable E_H-pH diagrams presented for cyanide and metal-complexed cyanides in Figures 2.3 and 2.8-2.11, respectively. A comparison of these figures to Figure 2.1 shows that the valence and conductance bands are reversed; however, this is merely due to convention. The position of the bands concurs with those determined at pH 1, 7, and 14 and illustrates that the bandgap for anatase is 3.2 eV

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(Ref. 54-57). According to Equation 1, a photon must have a frequency of 7.75×10^{14} Hz in order for its absorbance to occur. This equates to a maximum wavelength of 387.5 nm, indicating that the 254 and 185 nm UV sources employed in this study was adequate for inducing solid photocatalysis (see Section 3 - Treatability). As previously noted, conductance and valence bands represent the affinity for electrons to be consumed (by holes) and donated (as excited electrons) and are therefore a measure of relative reduction and oxidation potentials, respectively. Because the predominant stability regions for metal-complexed cyanides, cyanide, cyanate, and nitrite lie below the valence band, they can undergo oxidation, as depicted in Reactions 10 through 13, by releasing electrons to photon-produced holes.
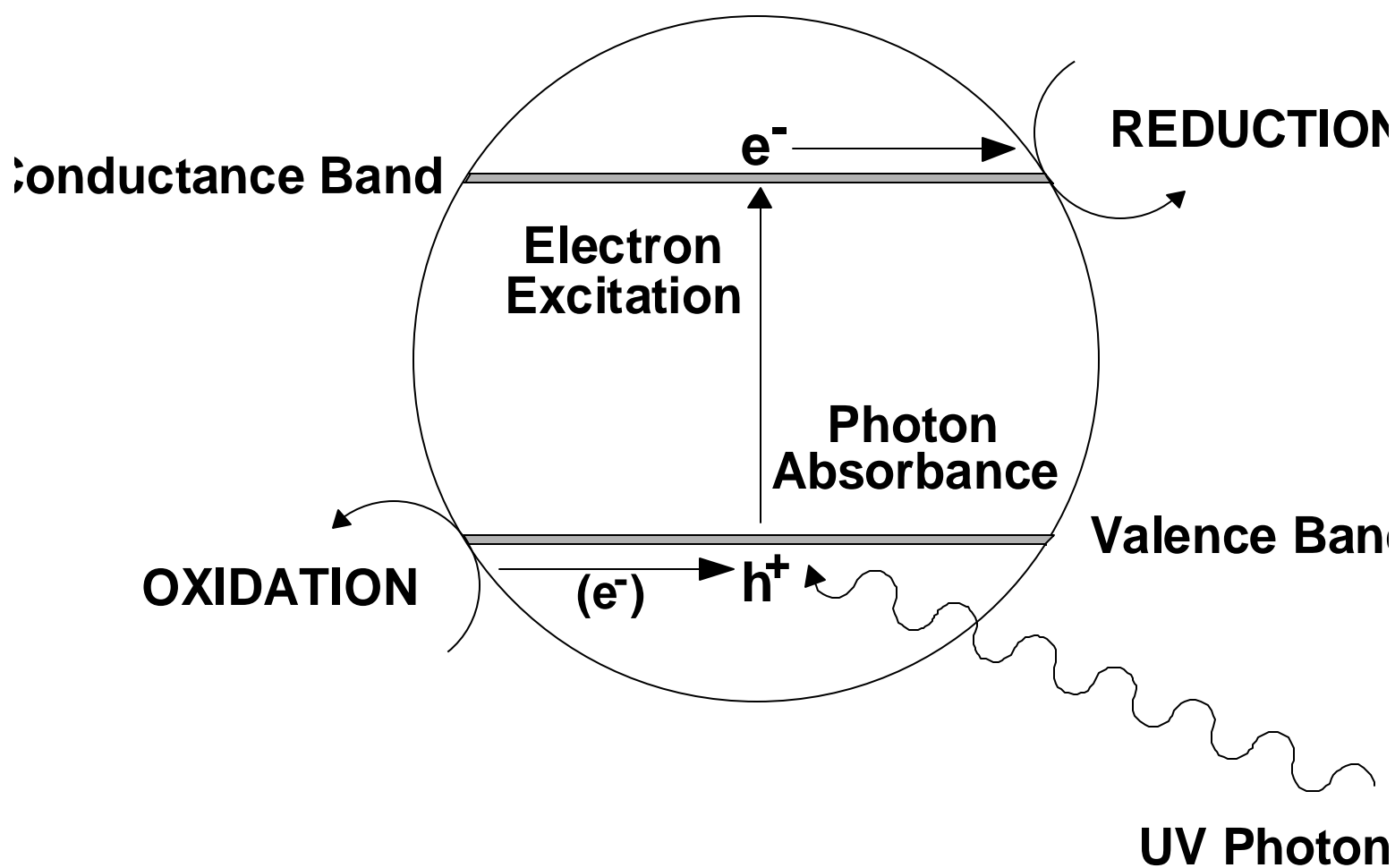
2-1. Schematic of UV-assisted redox reactions at the surface of solid photocatalysts.

S_1

S_0'

S_0

T

Photochemical Reaction

Intersystem Crossing

Absorbance

Rayleigh Scatter

Stokes Raman

Anti-Stokes Raman

Internal Conversion

Fluorescence

Phosphorescence
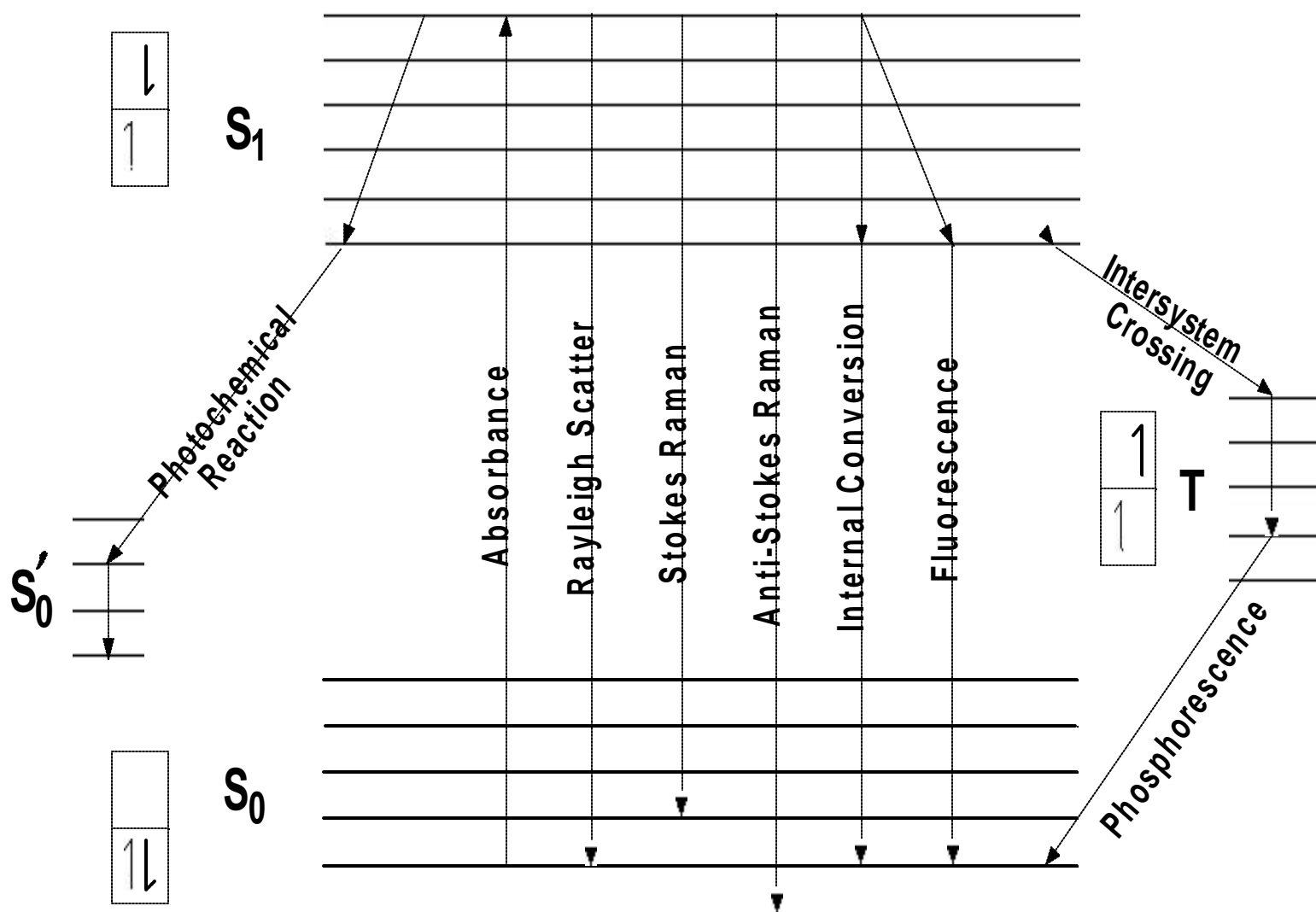
2-2. Jablonski energy-level diagram depiciting a direct UV –assisted chemical reaction.
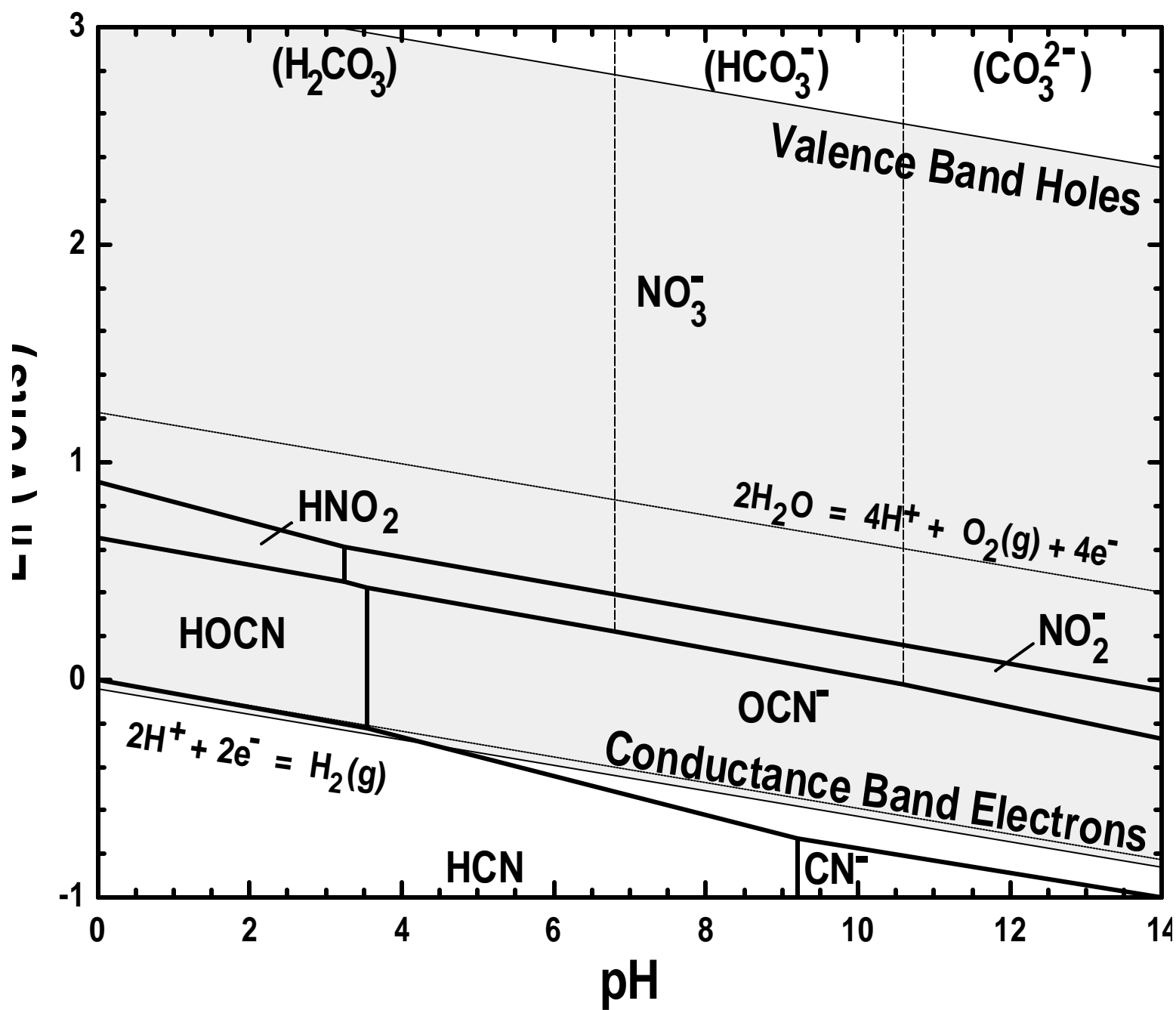
3-3. Stable carbon-nitrogen E_H-pH diagram in the absence of nitrogen gas illustrating cyanide oxidation to cyanate, nitrite, and nitrate.
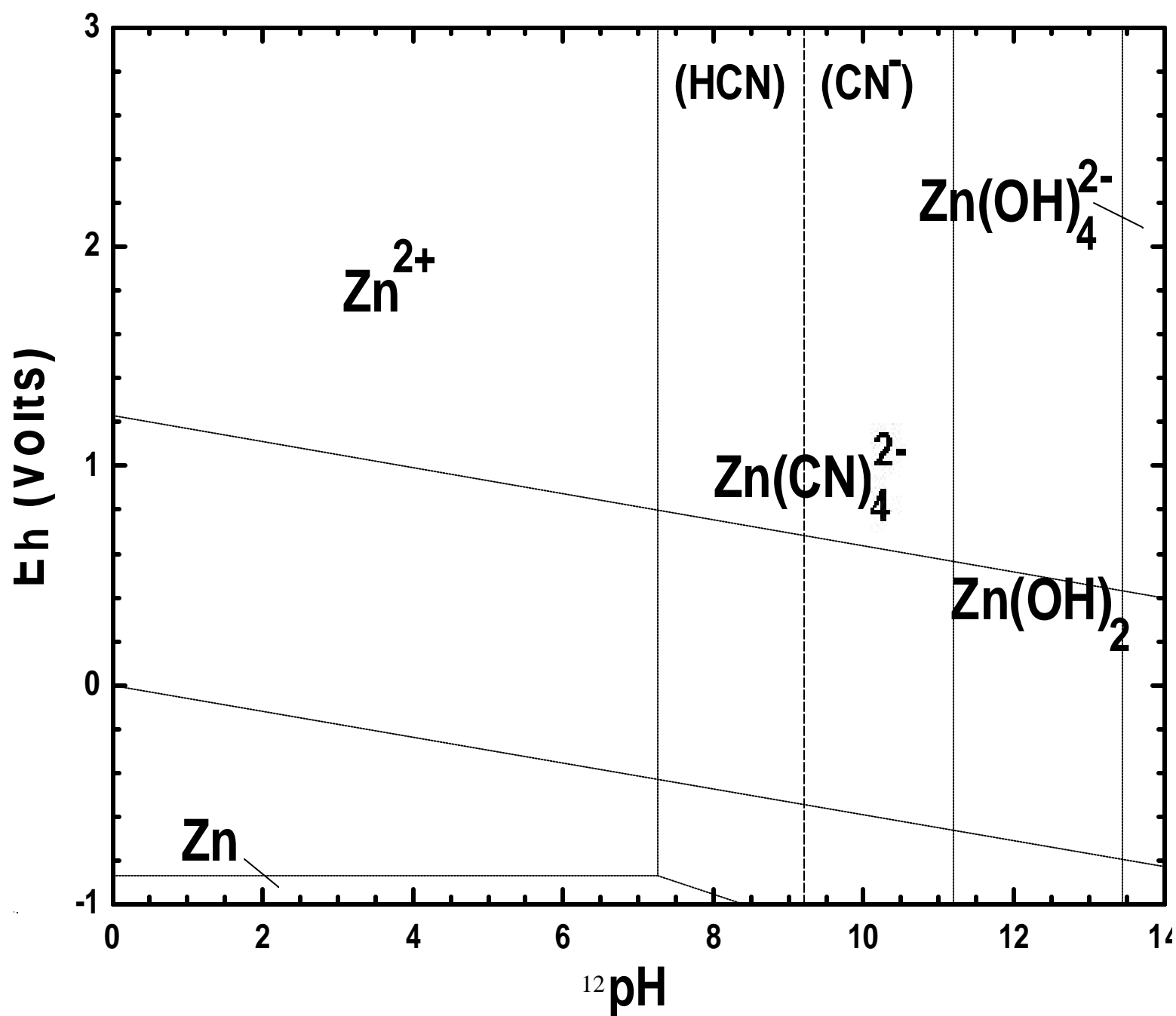
2-4. Metastable zink-carbon-nitrogen E_H-pH diagram.

(HCN) (CN^-)

Fe^{3+}

$Fe(OH)_3$

$Fe(CN)_6^{3-}$

$HFe(CN)_6^{3-}$

Fe^{2+}

$Fe(CN)_6^{4-}$

Fe

pH
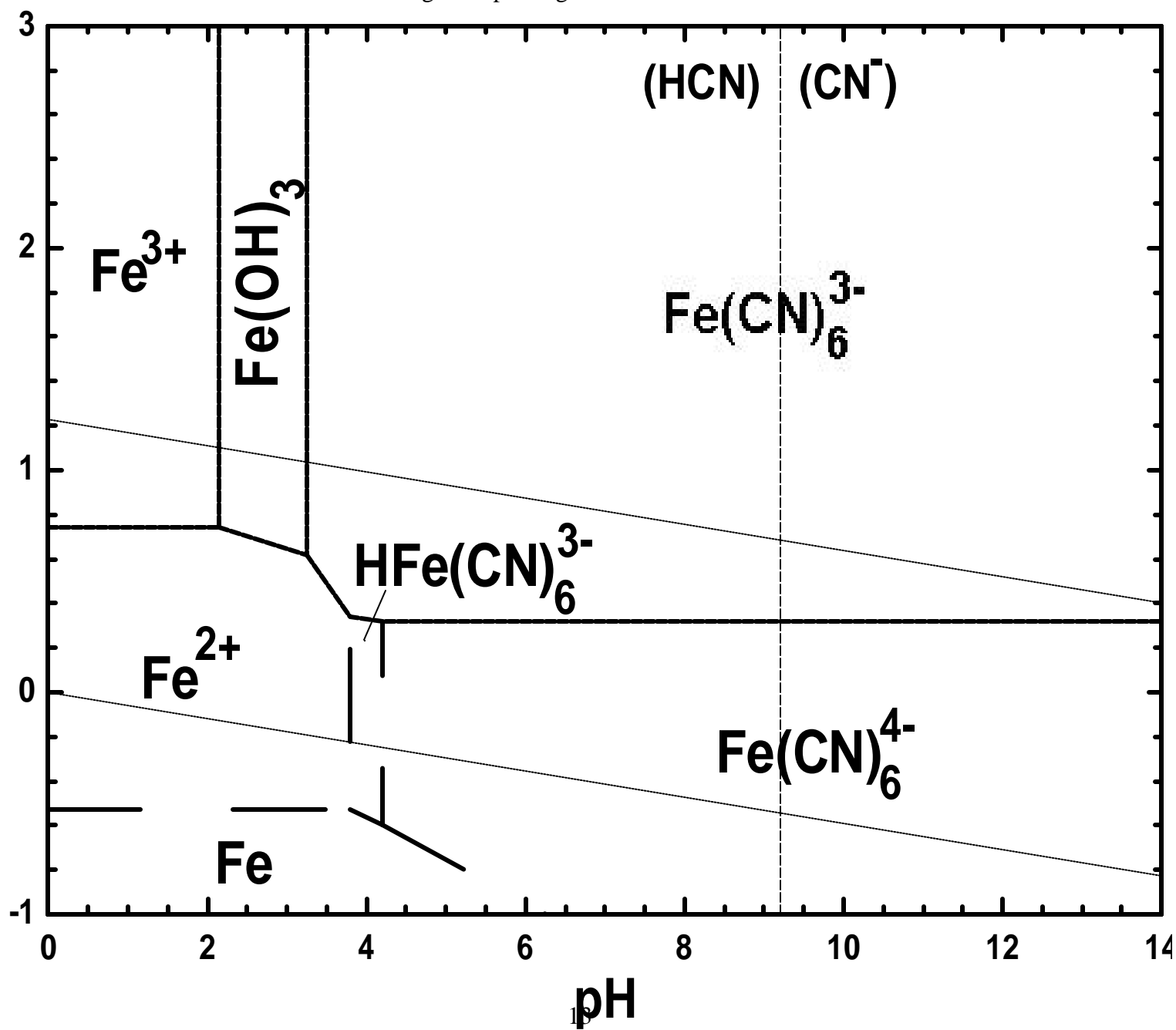
2-5. Netastable iron-carbon-nitrogen E_H-pH diagram.

(HCN) (CN⁻)

Au(OH)$_3$

Au^{3+}

HAuO$_3^{2-}$

Au(CN)$_2^-$

Au

Eh (VOItS)

3

2

1

0
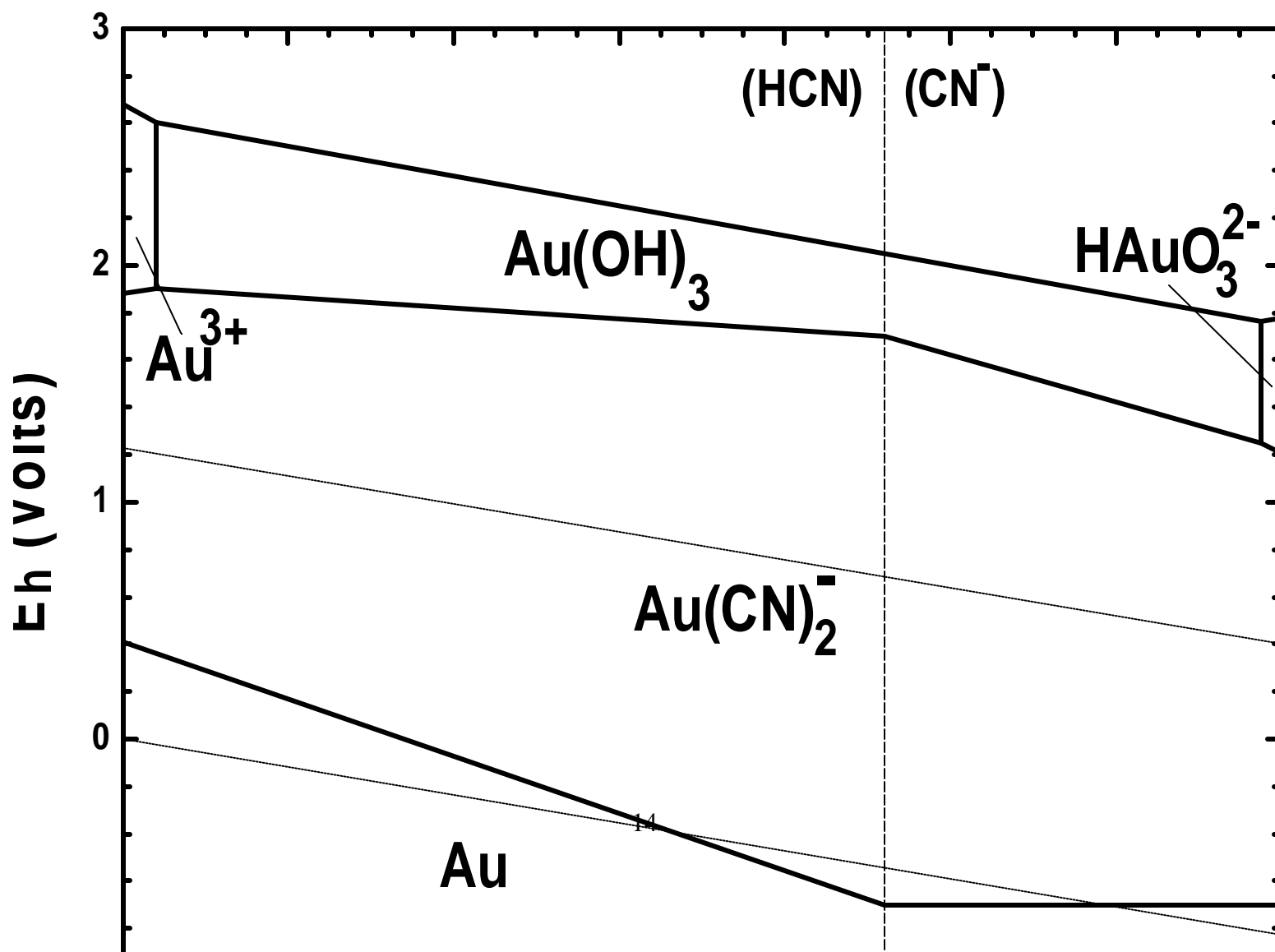
2-6/ Metastable gols-carbon-nitrogen E_H-pH diagram.

Co^{3+}

(HCN)   (CN$^-$)

Co(CN)$_6^{3-}$

Co^{2+}

Co(OH)$_2$

15

Co(CN)$_5^{3-}$

Eh (volts)

3

2

1

0

2-7. Meatstable cobalt-carbon-nitrogen E_H-pH diagram.

Zn^{2+}

$Zn(OH)_4^{2-}$

$Zn(OH)_2$

Fe^{3+}

$Fe(OH)_3$

Fe^{2+}

HFe(CN)$_6^{3-}$

FeOH$^+$

Fe(OH)$_2$

Eh (volts)

3

2

1

0
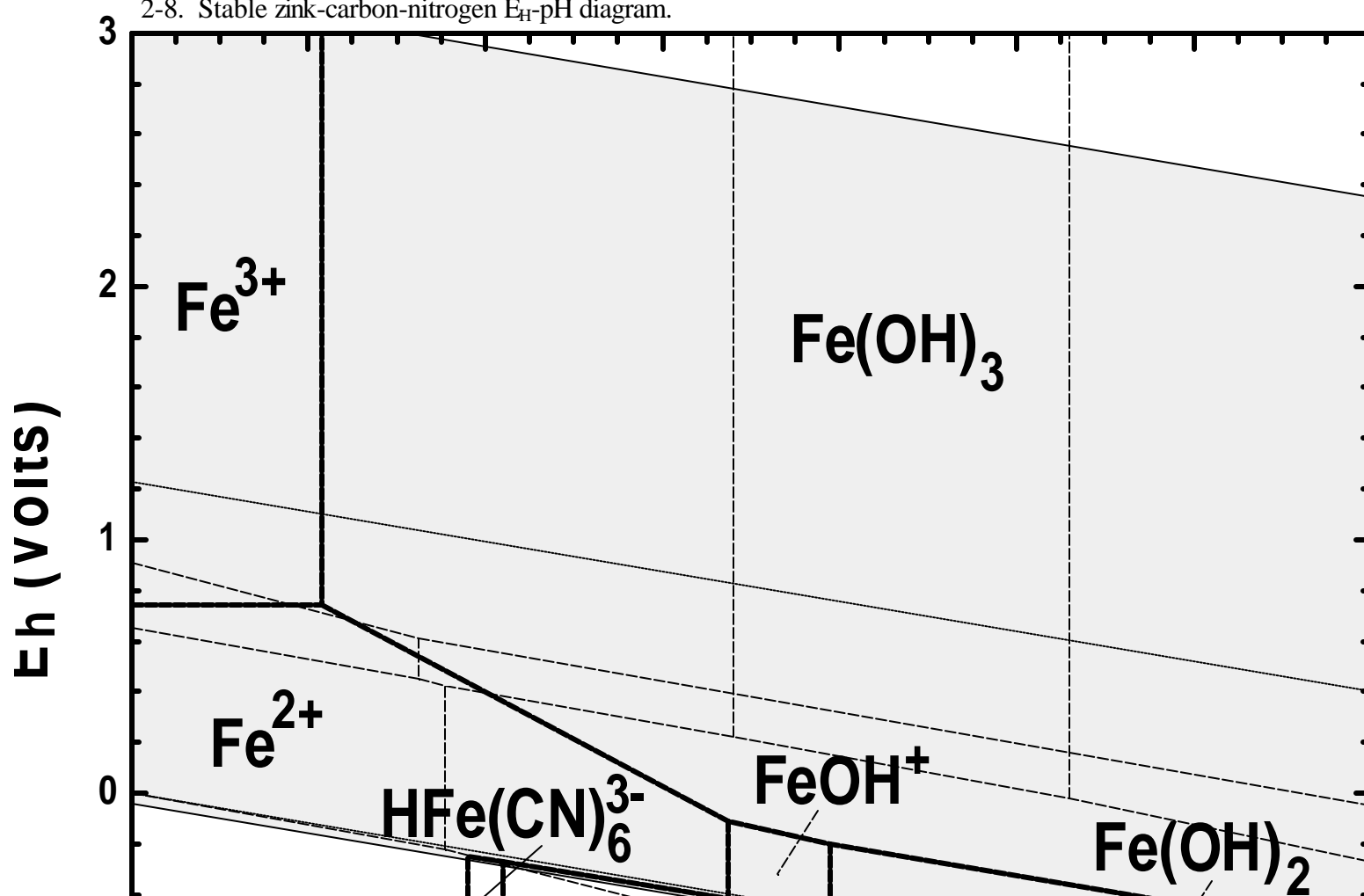
2-9. Stable iron-carbon-nitrogen E_H-pH diagram.

AuO_2

Au^{3+}

$Au(OH)_3$

$HAuO_3^{2-}$
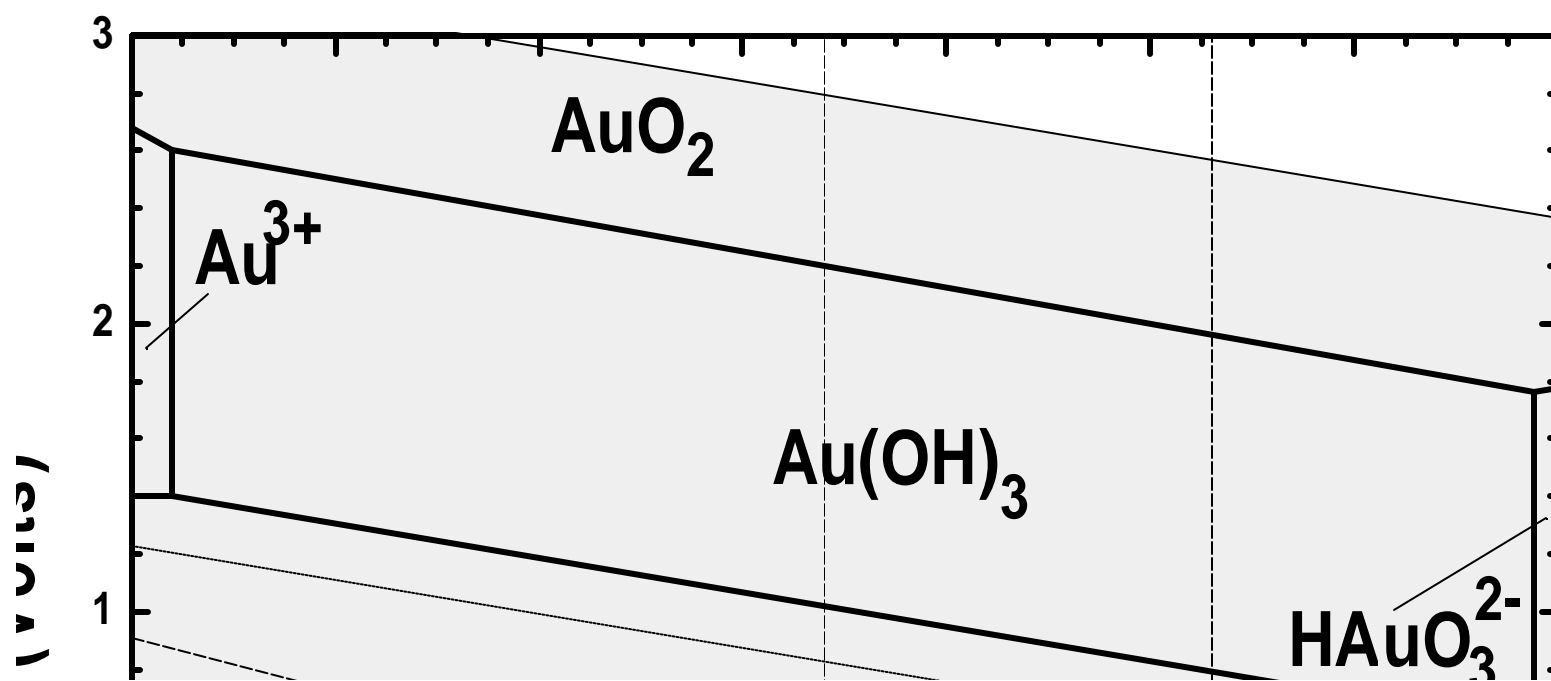
2-10. Stable gold-carbon-nitrogen E$_H$-pH diagram.

Co^{3+}

Co^{2+}

Co(OH)$_3$
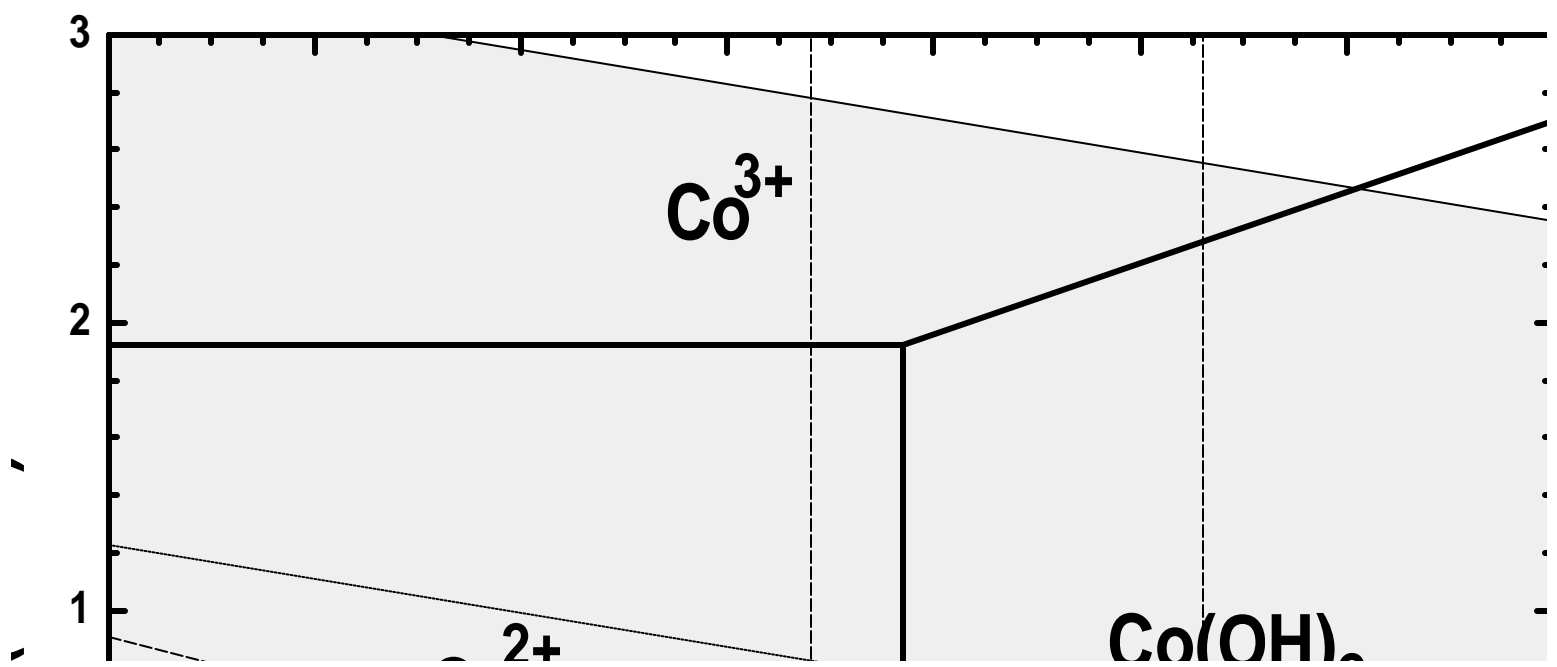
2-11. Stable cobalt-carbon-nitrogen E_H-pH diagram.

3. TREATABILITY

Experimental procedures were the same in this study as for the cyanide photooxidation experiments conducted in the previous MWTP study (Ref. 1). A major difference was in how the metal-cyanide complexes were detected and quantified and that an outside company, ACZ Laboratories, Inc. was used.

3.1 General Test Procedures

Sample solutions of 200 milliliter (ml) volume were prepared in standard 250 ml Pyrex beakers (Fisher) using deionized/distilled (DI) water with a concentration of metal-complexed cyanide (Coleman and Bell) equivalent to $6x10^{-3}$ M free cyanide (see Section 6 - Field Samples). In this regard, for example, $Au(CN)_2^-$ would have a concentration 3 times that of $Co(CN)_6^{3-}$ but, due to the difference in cyanide molar equivalent, their concentrations in free cyanide would be the same. Furthermore, this concentration is equivalent to 156 ppm CN^- and is approximate to the typical concentration of metal-complexed cyanide observed in the literature for cyanide wastewaters. After inserting Teflon-coated magnetic stirbars (VWR) in the solutions, the beakers were placed on magnetic stirrers (VWR) operating at approximately 2-speed and positioned in a chemical hood directly below UV sources (UVP, Inc.) with rated intensities of 3000 FW/cm^2. The UV sources emitted radiation at wavelengths between 120 nm and 280 nm with peak intensities centered at 185 and 254 nm. Tests were conducted in the absence and presence of a reagent grade photochemical, hydrogen peroxide, H_2O_2 (J.T. Baker) and a solid photocatalyst, anatase, TiO_2 (Degussa P25). Figure 3.1 depicts the experimental set-up.

QA/QC was conducted at all times (see Ref. 3 as well as Section 4 - Quality Assurance/Quality Control; and Section 6 - QA/QC Activities). Reagent schedules for the 10 UV-catalyzed QA/QC experiments are listed in Table 3.1. These experiments were found to be the most desirable after determining that the most appropriate photolytic technologies involved dissolved photosensitizers and solid photocatalysts as suggested by resulting publications and presentations from this project and Project 3 (Ref. 12,13,38,83-86). This includes the work of three undergraduate students in Metallurgical Engineering (Ref. 85,86).

In order to prevent pH drop due to the progression of the photooxidation reactions (see Reactions 10-13), the metal-complexed cyanide solutions were maintained at pH 11 using NaOH (Fischer) as determined with an Orion combination pH electrode (Model 81-02) and pH meter (Model 920A). This was in accordance with EPA Method number 4500-H$^+$, pH Electrometric Measurement (Ref. 87). The solutions were continuously sparged with oxygen gas to maximize oxidizing conditions. Metal-complexed cyanide concentrations were measured using a cyanide distillation apparatus (VWR). Caustic solution at pH 13 (0.1 M NaOH) was used to capture the distilled hydrogen cyanide gas. Cyanide concentrations in the caustic bath were measured with an Orion cyanide-ion selective electrode (Model 94-06) coupled to an Orion reference electrode (Model 90-02 res) and the above pH Meter. This was in accordance with EPA Method number 4500-CN$^-$ C, Total Cyanide After Distillation, and a modified 4500-CN$^-$ F, Cyanide Selective Electrode Method (Ref. 87). Aliquots were also taken to measure for the appearance of nitrate and nitrite using a Dionex DX-100 ion chromatograph (Model DX 1-03) equipped with an IONPAC**7** AS4A analytical column (P/N 37041), an IONPAC**7** AG4A guard column (P/N 30742), and an ion self suppressor (P/N 43189). This was in accordance with EPA Method 300.0, The Determination of inorganic Anions in Water by Ion Chromatography (Ref. 88). All aliquot samples were taken with 1-ml or 10-ml syringes (Fischer) equipped with 0.3 micron filters (Fischer). Prior to analysis, the aliquots were temporarily stored in 20-ml plastic vials (Fischer). Aliquots for the cyanide still and the ion chromatograph were only taken after 5 hours at the conclusion of the test. Experiments were simultaneously conducted in the dark to assess the applicability of UV

radiation (see Table 3.2).

3.2 Experimental Results

Metal-Complexed Cyanide photo-oxidation data is listed in Appendix B. The experiments were conducted at Montana Tech. However, due to problems associated with the detection of metal-complexed cyanides by distillation (see QA/QC Activities), the resulting solutions were analyzed by ACZ Laboratories, Inc. In this regard, the QA summary provided by ACZ Laboratories, Inc. is provided in Appendix C. The results are duplicated in Tables 3.3 and 3.4 and additionally presented as % Remediation:

$$\% \text{ Remediation} = ([\text{Original}] - [\text{Final}])/[\text{Original}] \qquad [14]$$

where [Original] and [Final] refer to the metal-complexed cyanide concentration at the start and after 5 hours. Negative values were reported as 0%. It is important to note that the UV-irradiated samples were done in duplicate thereby explaining why two values are reported for each test in Table 3.3. Ensuing discussions will be predominantly based on the % remediation calculation; however, it is important to note that all duplicate experiments were found to have passed QA/QC criteria using the equation for precision or relative percentage difference (RPD):

$$\text{RPD} = 100*(U-C)/[(U+C)/2] \qquad [15]$$

where U is assumed to be the measured (initial) concentration and C is assumed to be the actual (initial) concentration. To be acceptable, RPD-values must be less than 25% of the absolute value.

It was expected that the initial concentrations of each of the metal-complexed cyanide solutions would be 156 ppm (see Tables 3.3 and 3.4). It is quite clear that the measurements for the Zn-, Au- and Co-complexes were not. A re-examination of the experimental notes showed that the wrong weights were calculated for the Zn- and Au-complexes but not the Co-complex. Reasons for these mishaps follow. (1) In the QA/QC plan (Ref. 3), $Cu(CN)_2^-$ was going to be examined but CuCN(s) that was purchased to make it was found difficult to dissolve. Consequently, a decision was made to examine another weak acid dissociable (WAD), $Zn(CN)_4^{2-}$ (see QA/QC Activities). Unfortunately, the change in stoichiometry from 2 to 4 as well as the 80% purity of the $Zn(CN)_2$(s) used to make it was not taken into account. In this regard, an expected 156 ppm solution was actually expected to be 62.4 ppm and was found to measure 52 ppm. It is worth noting that that the only other chemical used in this study which was not >99% pure was $K_4Fe(CN)_6$ at 95% purity. Solutions of $Fe(CN)_6^{4-}$ were therfore expected to measure 148 ppm and found to measure 137 ppm. (2) In the case of the Au-complex, too many experiments were previously conducted thereby depleting the $KAu(CN)_2$(s) that was used. Enough sample existed for the work in this study if its concentration was halved (see QA/QC Activities). Consequently, a 78 ppm solution was expected and found to measure 84 ppm. (3) By comparison, it is quite clear that problems existed for quantifying the Co-complex concentration (see Appendices B and C). In this regard it is noted that (a) ACZ Laboratories, Inc. used an AllKem

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Rapid-Flow Analyzer (RFA) intrain colorimetric technique to analyze for total cyanide, (b) this technique appears to have difficulty with the refractoriness of $Co(CN)_6^{3-}$ as discussed earlier for the E_H-pH diagrams, and (c) as a result, the $Co(CN)_6^{3-}$ experiments appear that they would not pass QA/QC criteria.

In order to show that $Co(CN)_6^{3-}$ experiments did not pass QA/QC criteria, precision (Equation 15) and accuracy calculations were completed for all experiments. In this case, accuracy calculations refer to the use of the equation for recovery (R):

$$R = 100*(U/C) \hspace{4cm} [16]$$

where R is similar to calculations involving the analysis of spiked solutions. As before, U is assumed to be the measured (initial) concentration and C is assumed to be the actual (initial) concentration. To be acceptable, R-values must be between 75% and 125%. Table 3.6 shows that the $Co(CN)_6^{3-}$ experiments are the only experiments to fail these QA/QC criteria. Quite clearly, the AllKem Rapid-Flow Analyzer (RFA) intrain colorimetric procedure utilized by ACZ Laboratories, Inc. for $Co(CN)_6^{3-}$ detection did not pass QA/QC criteria. Further discussion regarding the $Co(CN)_6^{3-}$ results will therefore only be done in passing in the remainder of this report.

Additional examination of the results in Tables 3.3 and 3.4 shows that the metal-cyanide complexes are amenable to destruction by H_2O_2 but become more amenable to destruction when the H_2O_2/metal-complexed cyanide systems are exposed to UV radiation. $Fe(CN)_6^{3-}$ remediation increases from 12.7% to an average 32.1% when exposed to UV radiation. Likewise, $Au(CN)_2^{-}$ remediation increased from 21.4% to 32.8% and $Fe(CN)_6^{4-}$ remediation increased from 9.5% to 24.1%. Only $Zn(CN)_4^{2-}$ remediation was observed to decrease; however, the decrease from 99.4% to 98.3% is considered insignificant. These results suggest that hydrogen peroxidation (i.e., the DeGussa Process) may or may not be adequate for cyanide remediation depending on time constraints (i.e., 5 hours was used in this study) and on continuous additions at higher dosages (i.e., only one discrete addition of H_2O_2 was added and, perhaps, at too low of a dosage). In any case, it is clear that UV photolysis can improve upon the remediation of metal-complexed cyanides by the DeGussa Process.

Examination of the results obtained with TiO_2 shows that homogenous photocatalysis will not work unless UV radiation is used. Interestingly, TiO_2 photocatalysis only appeared to work for the Fe(II)-, Au- and Fe(III)- complexes which concurs with previous investigations (Ref. 37,40,49,85,86). However, the lack of $Zn(CN)_4^{2-}$ remediation is in disagreement (Ref. 85,86). An examination of the E_H-pH digrams presented earlier offers no explanation; however, it is conceivable that the Zn-complex did not adsorb at the TiO_2 surface. As discussed earlier, this is required for the process.

In this regard, it is important to note that, at pH 11 in which the experiments were conducted, TiO_2 would exhibit a negative surface charge (Ref. 89) that would repel similarly charged molecules if the surface bond, which would otherwise form, is not stronger. This coulombic behaviour has been noted

to play major roles in many adsorption systems. Furthermore, as discussed earlier, it has been postulated that UV-irradiated anatase produces hydroxyl radicals which then react to destroy toxic compounds. If this were the case, it would be expected that results would be independent of adsorption as well as the source of the hydroxyl radicals (i.e., hydrogen peroxide, etc.). Consequently, it is concluded that the mechanism for UV-irradiated anatase is a direct reaction with holes (h^+). The reaction for cyanide and metal complexed cyanides would be

$$CN^- + H_2O + 2h^+ = OCN^- + 2H^+ \qquad\qquad [17]$$
$$M(CN)_x^{y-x} + xH_2O + 4yh^+ = xOCN^- + 2xH^+ + M^{y+} \qquad\qquad [18]$$
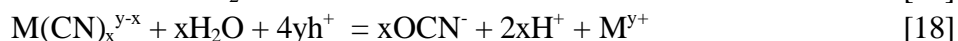
A comparison to Reactions 10 and 13 show that these reactions do not involve electrons. Clearly, adsorption is still a prerequisite for remediation to occur. However, depending on the redox chemistry, the metal cation product could precipitate as a hydroxide, oxide or metal and thereby passivate the anatase surface and reduce its photoreactivity.

Results of non-critical measurements of nitrite and nitrate concentrations via Ion Chromatography are shown in Appendix D. Results show that nitrite concentrations tended to be higher when hydrogen peroxide was used without irradiation (compared to with radiation) or when hydrogen peroxide was used with radiation (compared to irradiated anatase).   Because the appearance of nitrate and nitrite is a direct correlation to cyanide destruction, a remediation percentage can also be calculated assuming cyanate is not terminal reaction product (see Reactions 10-12) and, therefore, that the amount of cyanide remediation is equivalent to the sum of the amount of nitrite and nitrate which are produced. As can be seen, the remediation percentages are predominantly the same as those presented earlier in Tables 3.3 and 3.4. Only a few remediation percentages are different and seemingly always lower than respective values in Tables 3.3 and 3.4. This can be attributed to cyanate forming as a final product.

Lastly, due to the difficulties in measuring $Co(CN)_6^{3-}$ concentrations as well as the reasonably good correlation between the remediation of the other metal-complexed cyanides and the appearance of nitrite and nitrate, it is possible that the remediation values, especially those of $Co(CN)_6^{3-}$, presented in Appendix D are more accurate than those determined with the AllKem Rapid-Flow Analyzer (RFA) intrain colorimetric procedure by ACZ Laboratories, Inc. In order to show their was a good correlation between the direct (i.e., the results of ACZ Laboratories, Inc.) and indirect (the results in Appendix D) methods of calculating remediation percentages, precision calculations were made utilizing Equation 15. According to Tables 3.7 and 3.8, it is clear that only the $Co(CN)_6^{3-}$ tests failed to have good correlation. However, one $Zn(CN)_4^{2-}$ test also gave too large of a precision and can be attributed to the average of concentrations determined directly by ACZ Laboratories, Inc.

3.3 Summary
In this study, E_H-pH diagrams were constructed for cyanide complexes of Zn, Fe, Au and Co. These metals were selected due to their differences in cyanide bond strength; the stronger the bond, the less amenable the complex is to acid volatilization (i.e. distillation). In this regard, $Zn(CN)_4^{2-}$ exhibits one of

the weakest bonds and is therefore referred to as a weak acid disociable (WAD) whereas $Co(CN)_6^{3-}$ contains among the strongest and is referred to as a strong acid disociable (SAD). For the most part, resulting metastable E_H-pH diagrams verified this acid volatilization behavior; $Zn(CN)_4^{2-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{4-}$ and $Au(CN)_2^{-}$ were shown to volatilize (i.e. shown to be thermodynamically unstable) at pH values below 7.2, 3.7, 3.2, 0.2 and <0, respectively. However, when compared to stable E_H-pH diagrams in which the cyanide was allowed to oxidize to form cyanate, nitrite and nitrate, none of the metal-complexed cyanides were found to be stable in water. Photolysis is believed to overcome the energy barrier which makes the complexes stable in water thereby causing their destruction. In this regard, this study was undertaken, specifically to examine the effect of UV-irradiation on systems in the absence and presence of photolytic reagents such as hydrogen peroxide for homogeneous photolysis and anatase for heterogeneous photocatalysis. It is important to note that this study denotes the first time that an E_H-pH diagram has been constructed for the cobalt-cyanide-water system.

After experiments were conducted, EPA-approved QA/QC procedures were used to measure the concentrations of metal-complexed cyanides. Most measurements by this technique yielded data which was borderline acceptable, however, $Co(CN)_6^{3-}$ proved impossible due to its refractoriness. Subsequently, samples were prepared and delivered for analysis by an outside company, ACZ Laboratories, Inc., who used an AllKem Rapid-Flow Analyzer (RFA) intrain colorimetric procedure to analyze for total cyanide. Results showed this procedure also had difficulty in passing QA/QC. Clearly, an analytical method for accurately measuring the concentrations of metal-complexed cyanide, especially $Co(CN)_6^{3-}$, is needed.

It was found that the quantification of nitrite and nitrate reaction products would be adequate for indirectly determining its remediation due to excellent correlation with the remediation of other metal-complexed cyanides. In this regard, Table 3.9 is presented to show, within reason, results which likely would have been obtained. Table 3.9 is basically a composite of the results obtained from the direct metal-complexed cyanide measurements from ACZ LAboratories, Inc. or the indirect nitrite and nitrate measurements from Montana Tech. All results were rounded to the nearest five. It is important to note that the nitrite and nitrate concentrations were measured with an EPA-approved proceduare with ion chromatography but the measurements were not subjected to QA/QC protocol since they were deemed non-critical measurements.

Hydrogen peroxide alone can be adequate for remediating metal-complexed cyanides (the DeGussa Process) but becomes enhanced when UV-irradiated. On the other hand, anatase is only effective in the presence of UV radiation. Hydrogen peroxide tended to yield less nitrite when exposed to UV. Anatase was seeming most photo-efficient as it tended to yield the least amount of nitrite. Further comparison of the two photolytic processes indicates that, Aunder the conditions examined,@ UV-irradiated hydrogen peroxide is the better for remediating Zn-, Fe(II)-, Au- and Fe(III)-complexes and UV-irradiated anatase was found to be better for the Co-complex. Generally, this means WADs need only be remediated by homogeneous photolysis but SADs would require heterogeneous photocatalysis

for their destruction. In addition, because it has been proposed that UV-irradiated anatase produces hydroxyl radicals to destroy toxic compounds, it would be expected that results obtained by the UV-irradiation of both anatase and hydrogen peroxide would be the same (i.e., independent of adsorption as well as the source of the hydroxyl radicals). Consequently, it is concluded that the mechanism for UV-irradiated anatase is a direct reaction with holes (h^+):

$$CN^- + H_2O + 2h^+ = OCN^- + 2H^+$$
$$M(CN)_x^{y-x} + xH_2O + 4yh^+ = xOCN^- + 2xH^+ + M^{y+}$$
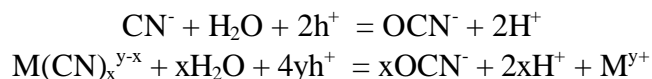
Clearly, adsorption is still a prerequisite for remediation to occur by anatase; however, in order to maximize its photoreactivity, the redox chemistry would have to be adjusted to avoid the precipitation of the metal as a hydroxide, oxide or metal and thereby prevent surface passivation. In this regard, further research is necessary because only one pH condition was investigated in this study. Lower pH conditions have shown increased reaction rates and therefore improved remediation efforts of free cyanide (Ref. 1). Furthermore, in regards to heterogeneous photocatalysis, a change in pH could also maximize adsorption onto the surface of anatase particles and simultaneously prevent the formation of precipitates.

UV Source

Gas

Electrode

Glass Frit

Magnet

Magnetic Stirrer
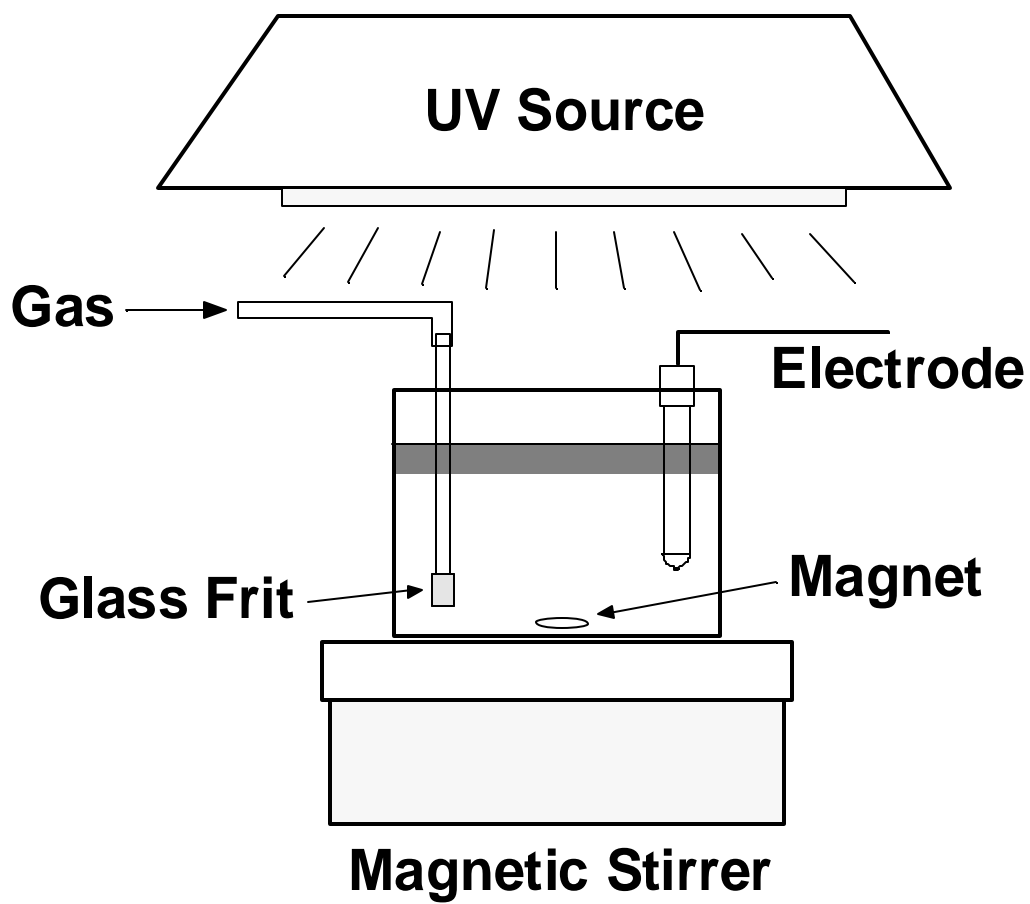
3-1. Experimental setup for metal-comlexed cyanide shoto-oxidation tests.

Table 3.1 UV-Irradiated Metal-Complexed Cyanide Test Solutions and Reagent Schedules

Sample No.	Sample Reagent Concentration (M)		Photolytic Reagent Concentration (M or g/l)		Sparging Gas
1	$Zn(CN)_4^{2-}$	0.0015 M	30% H_2O_2	5 ml	O_2
2	$Fe(CN)_6^{4-}$	0.001 M	30% H_2O_2	5 ml	O_2
3	$Au(CN)_2^{-}$	0.003 M	30% H_2O_2	5 ml	O_2
4	$Fe(CN)_6^{3-}$	0.001 M	30% H_2O_2	5 ml	O_2
5	$Co(CN)_6^{3-}$	0.001 M	30% H_2O_2	5 ml	O_2
6	$Zn(CN)_4^{2-}$	0.0015 M	TiO_2	1.5 g/l	O_2
7	$Fe(CN)_6^{4-}$	0.001 M	TiO_2	1.5 g/l	O_2
8	$Au(CN)_2^{-}$	0.003 M	TiO_2	1.5 g/l	O_2
9	$Fe(CN)_6^{3-}$	0.001 M	TiO_2	1.5 g/l	O_2
10	$Co(CN)_6^{3-}$	0.001 M	TiO_2	1.5 g/l	O_2

Table 3.2 Non-Irradiated Metal-Complexed Cyanide Test Solutions and Reagent Schedules

Sample No.	Sample Reagent Concentration (M)		Photolytic Reagent Concentration (M or g/l)		Sparging Gas
11	$Zn(CN)_4^{2-}$	0.0015 M	30% H_2O_2	5 ml	O_2
12	$Fe(CN)_6^{4-}$	0.001 M	30% H_2O_2	5 ml	O_2
13	$Au(CN)_2^{-}$	0.003 M	30% H_2O_2	5 ml	O_2
14	$Fe(CN)_6^{3-}$	0.001 M	30% H_2O_2	5 ml	O_2
15	$Co(CN)_6^{3-}$	0.001 M	30% H_2O_2	5 ml	O_2
16	$Zn(CN)_4^{2-}$	0.0015 M	TiO_2	1.5 g/l	O_2
17	$Fe(CN)_6^{4-}$	0.001 M	TiO_2	1.5 g/l	O_2
18	$Au(CN)_2^{-}$	0.003 M	TiO_2	1.5 g/l	O_2
19	$Fe(CN)_6^{3-}$	0.001 M	TiO_2	1.5 g/l	O_2

20	$Co(CN)_6^{3-}$	0.001 M	TiO_2	1.5 g/l	O_2

Table 3.3 % Remediation of UV-Irradiated Metal-Complexed Cyanide Test Solutions

Sample No.	Metal Complex	Photolytic Reagent	Initial Conc. (ppm)	Final Conc. (ppm)		% Remediation	
1	$Zn(CN)_4^{2-}$	H_2O_2	52	0.7	0.9	98.7	98.3
2	$Fe(CN)_6^{4-}$	H_2O_2	137	98	110	28.5	19.7
3	$Au(CN)_2^{-}$	H_2O_2	84	69	44	17.9	47.6
4	$Fe(CN)_6^{3-}$	H_2O_2	165	116	108	29.7	34.5
5*	$Co(CN)_6^{3-}$	H_2O_2	4.0	5.0	4.0	0	0
6	$Zn(CN)_4^{2-}$	TiO_2	52	52	67	0	0
7	$Fe(CN)_6^{4-}$	TiO_2	137	123	141	10.2	0
8	$Au(CN)_2^{-}$	TiO_2	84	90	67	0	20.2
9	$Fe(CN)_6^{3-}$	TiO_2	165	124	117	24.8	29.1
10*	$Co(CN)_6^{3-}$	TiO_2	4.0	2.4	1.7	40.0	57.5

* did not pass QA/QC criteria

Table 3.4 % Remediation of Non-Irradiated Metal-Complexed Cyanide Test Solutions

Sample No.	Metal Complex	Photolytic Reagent	Initial Conc. (ppm)	Final Conc. (ppm)	% Remediation
11	$Zn(CN)_4^{2-}$	H_2O_2	52	0.3	99.4
12	$Fe(CN)_6^{4-}$	H_2O_2	137	124	9.5
13	$Au(CN)_2^{-}$	H_2O_2	84	66	21.4
14	$Fe(CN)_6^{3-}$	H_2O_2	165	144	12.7
15*	$Co(CN)_6^{3-}$	H_2O_2	4.0	1.5	62.5
16	$Zn(CN)_4^{2-}$	TiO_2	52	99	0

17	$Fe(CN)_6^{4-}$	TiO_2	137	129	5.8
18	$Au(CN)_2^-$	TiO_2	84	82	2.4
19	$Fe(CN)_6^{3-}$	TiO_2	165	182	0
20*	$Co(CN)_6^{3-}$	TiO_2	4.0	1.8	55.0

* did not pass QA/QC criteria

Table 3.5 Quality Indicator for Duplicate Experiments

Sample No.	Metal Complex	Photolytic Reagent	Duplicate A Conc. (ppm)	Duplicate B Conc. (ppm)	% Precision
1	$Zn(CN)_4^{2-}$	H_2O_2	0.7	0.9	12.5
2	$Fe(CN)_6^{4-}$	H_2O_2	98	110	5.8
3	$Au(CN)_2^-$	H_2O_2	69	44	22.1
4	$Fe(CN)_6^{3-}$	H_2O_2	116	108	3.6
5	$Co(CN)_6^{3-}$	H_2O_2	5.0	4.0	11.1
6	$Zn(CN)_4^{2-}$	TiO_2	52	67	12.6
7	$Fe(CN)_6^{4-}$	TiO_2	123	141	6.8
8	$Au(CN)_2^-$	TiO_2	90	67	14.6
9	$Fe(CN)_6^{3-}$	TiO_2	124	117	2.9
10	$Co(CN)_6^{3-}$	TiO_2	2.4	1.7	17.1

Table 3.6 Quality Indicators for the Actual and Measured Initial Concentrations

Sample No.=s	Metal Complex	Actual Initial Conc. (ppm)	Measured Initial Conc. (ppm)	% Accuracy	% Precision
1, 6, 11 & 16	$Zn(CN)_4^{2-}$	62.4	52	83.3	18.2
2, 7, 12 & 17	$Fe(CN)_6^{4-}$	148	137	92.6	7.7
3, 8, 13 & 18	$Au(CN)_2^-$	78	84	108.7	7.4
4, 9, 14 & 19	$Fe(CN)_6^{3-}$	156	165	105.8	5.6

| 5, 10, 15 & 20 | $Co(CN)_6^{3-}$ | 156 | 4.0 | 2.6* | 190.0* |

* did not pass QA/QC criteria

Table 3.7 Quality Indicator for Direct and Indirect Final Cyanide Concentration Measurements of UV-Irradiated Experiments

Sample No.	Metal Complex	Photolytic Reagent	Average Direct Conc. (ppm)	Initial Conc. (ppm)	Average Equivalent Conc. (ppm)	Indirect Conc. (ppm)	% Precision
1	$Zn(CN)_4^{2-}$	H_2O_2	0.8	62.4	61.55	0.85	6.1
2	$Fe(CN)_6^{4-}$	H_2O_2	104	148	26.9	121.1	15.2
3	$Au(CN)_2^{-}$	H_2O_2	56.5	78	31.2	46.8	18.8
4	$Fe(CN)_6^{3-}$	H_2O_2	112	156	54.85	101.15	10.2
5	$Co(CN)_6^{3-}$	H_2O_2	4.5	156	6.82	149.18	188
6	$Zn(CN)_4^{2-}$	TiO_2	59.5	62.4	2.035	60.365	1.4
7	$Fe(CN)_6^{4-}$	TiO_2	132	148	13.85	134.15	1.61
8	$Au(CN)_2^{-}$	TiO_2	78.5	78	11.65	66.35	16.8
9	$Fe(CN)_6^{3-}$	TiO_2	120.5	156	28.8	127.2	5.4
10	$Co(CN)_6^{3-}$	TiO_2	2.05	156	13.85	142.15	194

Table 3.8 Quality Indicator for Direct and Indirect Indirect Final Cyanide Concentration Measurements of Non-Irradiated Experiments

Sample No.	Metal Complex	Photolytic Reagent	Average Direct Conc. (ppm)	Initial Conc. (ppm)	Average Equivalent Conc. (ppm)	Indirect Conc. (ppm)	% Precision
11	$Zn(CN)_4^{2-}$	H_2O_2	0.3	62.4	62.1	0.3	0
12	$Fe(CN)_6^{4-}$	H_2O_2	124	148	15.6	132.4	6.6
13	$Au(CN)_2^{-}$	H_2O_2	66	78	16.3	61.7	6.7

14	$Fe(CN)_6^{3-}$	H_2O_2	144	156	35.1	120.9	17.4
15	$Co(CN)_6^{3-}$	H_2O_2	1.5	156	3.67	152.33	196
16	$Zn(CN)_4^{2-}$	TiO_2	99	62.4	0.62	61.78	46.3
17	$Fe(CN)_6^{4-}$	TiO_2	129	148	0.53	147.47	13.4
18	$Au(CN)_2^{-}$	TiO_2	82	78	0.63	77.37	5.8
19	$Fe(CN)_6^{3-}$	TiO_2	182	156	0.73	155.27	15.9
20	$Co(CN)_6^{3-}$	TiO_2	1.8	156	0.99	155.01	195

Table 3.9 Estimated % Remediation Assuming Accurate Concentration Measurements

Metal-Complexed Cyanide	% Remediation with UV		% Remediation without UV	
	H_2O_2	TiO_2	H_2O_2	TiO_2
$Zn(CN)_4^{2-}$	100	5	100	0
$Fe(CN)_6^{4-}$	20	10	10	0
$Au(CN)_2^{-}$	35	15	20	0
$Fe(CN)_6^{3-}$	35	20	15	0
$Co(CN)_6^{3-}$	5	10	0	0

4. QA/QC

Major purposes of this MWTP project were identifying photolytic processes that could be used for the remediation of nitrate and cyanide in wastewaters and evaluating the processes to assess their scientific feasibility via determining reaction kinetics and products so that recommendations could be made to continue this research effort. The programmatic and regulatory setting in which the project quality assurance was conducted was Category III as outlined in MWTP Activity IV, Project 3A QAPP (Ref. 3). Projects are designated Category III when results are used to evaluate and select basic options or to perform feasibility studies or preliminary assessments of unexplored areas. Existing background data presented in Section 2 - Photochemistry was not required to conform to any criteria. This information is considered common knowledge since it was predominantly the foundation to the workplan (Ref. 2).

4.1 QA/QC Objectives
The Quality Assurance/Quality Control (QA/QC) objectives outlined for the project were specified to generate acceptable data. The MWTP Activity IV, Project 3A QAPP (Ref. 3) was provided to insure:
C   measurements were appropriate for achieving project objectives,
C   quality control procedures were sufficient for obtaining data of known and adequate quality, and
C   such data would be defensible if technically challenged.
Ultimately, it would be desirable to show that the selected photolytic technologies for metal-complexed cyanide remediation yielded concentrations below the U.S. EPA Drinking Water Standards of 200 ppb $(7.7 \times 10^{-6}$ M) CN^- (Ref. 22). However, as noted in the experimental procedures, a cyanide specific ion electrode with a detection limit of 8×10^{-6} M was used to measure the free cyanide concentration after distillation, quality-assured measurements below the Drinking Water Standard could not be determined. Nevertheless, project objectives were to identify and then evaluate appropriate photolytic processes that remediate metal-complexed cyanide in wastewaters, not necessarily achieve the Drinking Water Standard. This task would be reserved for future studies and accordingly recommended if such concentrations were obtained.

4.2   Analyses
Metal-complexed cyanide solutions were monitored for concentration and pH as well as for nitrate and nitrite concentrations. Only U.S. EPA-approved methods were employed.

4.2.1   Procedures
U.S. EPA-approved methods included pH Electrometric Measurement (Method No. 4500-H^+), Determination of Inorganic Anions in Water by Ion Chromatography (Method No. 300.0) for the nitrite and nitrate concentration measurements, and metal-complexed cyanide concentration measurements by distillation (Method No. 4500-CN^- C coupled with cyanide selective electrode measurement, Method No. 4500-CN-F-modified). Electrometric measurements for pH were conducted in the reaction vessel every hour and CN^- concentration were conducted in the absorption column of the distillation apparatus after 5 hours of equilibration. The pH was controlled at pH 11 for all experiments using drops from NaOH solutions, as needed. Nitrite and nitrate concentrations were determined by injecting 1 ml

aliquot samples into the ion chromatograph after having been taken at the conclusion of a test. Aliquots may have been stored temporarily in 20 ml plastic vials between measurements. Equipment manufacturers and types are specified in Section 3 - Treatability.

4.2.2 Calibrations

pH meter. Buffer solutions at pH 7.0 and 11.0 were used in the standard two-point calibration of the pH meter. The buffer pH values bracketed the pH 11 control that was used. The pH meter was recalibrated after every 20 measurements and at the conclusion of every test. Percent slopes were consistently found to be $100\% \pm 5\%$. Measurements of pH were non-critical to all tests.

Ion chromatograph. Before every test, a blank and three nitrite and nitrate standards were used to establish working curves between 0 and 250 ppm. This calibration range bracketed all nitrate and nitrite concentrations measured. Calibration curves were analyzed by PeakSimple data software (SRI Instruments) using R^2-correlation coefficients. In this regard, R^2-values typically measured 0.97 which was consistently greater than the 0.90 acceptance criterium. Although never encountered, the chromatograph was to be recalibrated if a standard, upon being checked after every 20th measurement, was outside 75-125% linear range. Nitrite and nitrate measurements were non-critical to all tests.

Cyanide still. The U.S. EPA-approved Cyanide After Distillation Method was modified only to accomodate the still size and the 50-ml aliquot amounts being analyzed. Reagent dosages of sulfamic acid, $MgCl_2$ and H_2SO_4 were therefore proportioned. This procedure was abandoned when difficulties analyzing for $Co(CN)_6^{3-}$ were obtained (see QA/QC Activities) in favor of an outside company, ACZ Laboratories, Inc. Metal-complexed cyanide concentration measurements were critical to all tests.

Cyanide electrode. The U.S. EPA-approved Cyanide Selective Electrode Measurement Method was modified to a 3-point calibration using a working curve from 2.5 to 250 ppm cyanide from the 4-point calibration with a working curve from 0.025 to 2.5 ppm cyanide. This calibration range bracketed all cyanide concentrations as the tests were allowed to progress. Slope values were recorded in millivolts (mV) and consistently found to be within acceptable criteria of 59.2 ± 7 mV. Although never encountered, the cyanide electrode was to be recalibrated if a standard, upon being checked after every 5th measurement, was outside 95-105% linear range. Cyanide-concentration measurements were critical to all metal-complexed cyanide tests; however, as noted above, this procedure was abandoned in favor of an outside company, ACZ Laboratories, Inc.

5. QA/QC CHECK PROCEDURES AND ACTIVITIES

5.1 Check Procedures

Numerous procedures were in place to assure that quality data was reported. These check procedures included

C   recalibrating the various instruments used through the course of the tests as described in Section 4 - Quality Assurance/Quality Control,

C   analyzing calibration standards periodically to assure the various instruments were functioning properly as also described in Section 4 - Quality Assurance/Quality Control,

C   measuring reagent blanks periodically to make sure the various instruments were not contaminated thereby giving false readings,

C   running a duplicate sample to assure the data was reproducible,

C   running a second duplicate sample in the dark to verify effects of UV radiation,

C   matrix-spiking a test to to assure the various instruments were functioning properly thereby yielding results within 75-125% recovery,

C   using laboratory fortified blanks for determining acceptable performance of the ion chromatograph,

C   establishing proficiency on the ion chromatograph by measuring 4 equally prepared aliquots, calculating average % recoveries, standard deviations, and upper and lower control limits, and by comparing results to values found in the accuracy and precision table found in Determination of Inorganic Anions in Water by Ion Chromatography (Method No. 300.0), and

C   analyzing the results obtained from an outside laboratory via quality indicator calculations.

Not all of these QA/QC check procedures passed. Corrective action which was taken is described in the ensuing section.

5.2 Activities

During the course of the QA/QC experiments, problems arose which required QA/QC activities. These activities included

C   having an outside company, ACZ Laboratories, Inc., measure the concentrations of the metal-complexed cyanide using another technique. This was due to the difficulties that Montana Tech had in getting SAD complexes, especially $Au(CN)_2^-$ and $Co(CN)_6^{3-}$, to distill and give a reasonable cyanide concentration measurement in the caustic trap solution. Because QA indicators failed, experiments were repeated several times as required by QA/QC procedures, but unsatisfactory results were always obtained,

C   examining a WAD species different from the $Cu(CN)_2^-$ complex that was proposed. This was necessary because of the difficulties encountered in getting CuCN(s) to dissolve and yield the $Cu(CN)_2^-$ complex that was wanted for examination. It was decided that the other WAD species would be $Zn(CN)_4^{2-}$. A request to EPA was made and granted in this regard,

C   lowering the concentration of $Au(CN)_2^-$ because not enough $KAu(CN)_2$ was remaining to complete the QA/QC study at the specified concentrations due to the need to repeat

experiments as noted above. In this regard, the amount of $KAu(CN)_2$ was halved,

C   removing nitrite and nitrate concentration measurements from the critical measurement list to the non-critical list since the results were deemed unimportant to the needs of the study. A request to EPA was made and granted in this regard but before it was realized that the outside company, ACZ Laboratories, Inc., would also have problems with concentration measurements of some metal-complexed cyanides, especially $Co(CN)_6^{3-}$, and

C   completing QA indicator calculations to verify that $Co(CN)_6^{3-}$ concentration measurements determined by ACZ Laboratories were flawed (see Section 3 - Treatability). However, in doing so, it was found that excellent correlation with nitrite and nitrate concentration measurements were obtained such that their concentrations could be summed and converted to equivalent cyanide concentrations. Unfortunately, the nitrite and nitrate concentrations were not critically measured as noted above.

6. CONCLUSIONS

6.1 Summary

In this study, E_H-pH diagrams were constructed for cyanide complexes of Zn, Fe(II), Fe(III), Au and Co under metastable and stable conditions. These metals were selected due to their differences in stability. For the most part, resulting metastable E_H-pH diagrams, in which the cyanide was not allowed to oxidize to form cyanate, nitrite and nitrate, showed $Zn(CN)_4^{2-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{4-}$ and $Au(CN)_2^-$ did not volatilize (i.e. shown to be thermodynamically unstable) at pH values below 7.2, 3.7, 3.2, 0.2 and <0, respectively. However, when compared to the stable E_H-pH diagrams in which the cyanide was allowed to oxidize, none of the metal-complexed cyanides were found to be stable in water. Photolysis is believed to overcome the energy barrier which makes the complexes stable in water thereby causing their destruction. In this regard, this study was undertaken, specifically to examine the effect of UV-irradiation on systems in the absence and presence of photolytic reagents such as hydrogen peroxide for homogeneous photolysis and anatase for heterogeneous photocatalysis. It is important to note that this study denotes the first time that an E_H-pH diagram was constructed for the cobalt-cyanide-water system.

After experiments were conducted, EPA-approved QA/QC distillation procedures were used to measure the concentrations of metal-complexed cyanides. Most measurements by this technique yielded data which was borderline acceptable, however, $Co(CN)_6^{3-}$ proved impossible due to its refractoriness. Consequently, samples were prepared and delivered for analysis by an outside company, ACZ Laboratories, Inc., who used an AllKem Rapid-Flow Analyzer (RFA) intrain colorimetric procedure to analyze for total cyanide. Various QA/QC indicators were calculated and and used to show that this procedure also had difficulty in passing QA/QC criteria. Clearly, an analytical method for accurately measuring the concentrations of metal-complexed cyanide, especially $Co(CN)_6^{3-}$, is needed.

It was found that the quantification of nitrite and nitrate reaction products would be adequate for indirectly determining its remediation due to excellent correlation with the remediation of other metal-complexed cyanides. In this regard, a table was constructed (see Table 3.9) from a composite of the results obtained from the direct metal-complexed cyanide measurements from ACZ LAboratories, Inc. and the indirect nitrite and nitrate measurements from Montana Tech to show, within reason, results which likely would have been obtained had a reliable technque been used.

Hydrogen peroxide alone can be adequate for remediating metal-complexed cyanides (the DeGussa Process) but becomes enhanced when UV-irradiated. On the other hand, anatase is only effective in the presence of UV radiation. Hydrogen peroxide tended to yield less nitrite when exposed to UV. Anatase was seeming most photo-efficient as it tended to yield the least amount of nitrite. Further comparison of the two photolytic processes indicates that, Aunder the conditions examined,@ UV-irradiated hydrogen peroxide is the better for remediating Zn-, Fe(II)-, Au- and Fe(III)-complexes and UV-irradiated anatase was found to be better for the Co-complex. Generally, this means WADs need

only be remediated by homogeneous photolysis but SADs would require heterogeneous photocatalysis for their destruction. Since the literature suggests that the remediation mechanism for both UV-irradiated anatase and hydrogen peroxide is due to the formation of hydroxide radicals, a theory which suggests results should be independent of the source of hydroxide radicals, a new meachanism for the remediation by homogeneous photocatalysis was proposed. This mechanism involves a reaction with holes (h^+) as opposed to a release of electrons (e^-).

However, it is critical to note that further research is necessary because only one pH condition was investigated in this study. Lower pH conditions have shown increased reaction rates and therefore improved remediation efforts of free cyanide. Furthermore, in regards to heterogeneous photocatalysis, a change in pH could also maximize adsorption onto the surface of anatase particles and simultaneously prevent the formation of precipitates of hydroxides, oxides and metals which, upon formation, could mask the anatase surface and thereby diminish its photoreactivity.

6.2 Recommendations

Because this study was principally modeled after the previous MWTP study on photolysis for remediating free cyanide, many of the recommendations made here are the same. In this regard, it is suggested that, because the photolytic technologies examined in this study are promising, they be further investigated to improve upon reaction efficiencies and/or reaction rates. This can be accomplished by examining other solid photocatalysts, other dissolved photosensitizers, initial concentrations, redox potential, sparging gases, temperatures, pH conditions, UV wavelengths, and UV intensities. For example,

C   ZnO, WO_3, CdS, SiC, Fe_2O_3, and certain zeolites, for examples, would be great photocatalysts to study,

C   nitrate (NO_3^-) and sulfite (SO_3^-) are examples of dissolved photosensitizers which yield hydroxyl radicals when exposed to UV radiation and therefore are good candidates for studying,

C SO_2, Ar, N_2, O_3, and CO_2 are excellent candidates for changing atmospheric conditions and simultaneously modifying the redox potential of the systems,

C   temperatures ranging from near-freezing to near-boiling should be examined to mimic changing conditions observed in cold and hot climates,

C   the effects of pH and other chemicals on adsorption need to be understood in order to determine maximum adsorption conditions and therefore determine maximum conditions in which cyanide destruction would occur, and

C   other wavelengths and intensities aside from the 254/185 nm and 600 FW/cm^2 used in this study are available and can be obtained from a variety of different sources including lamps, arcs and lasers.

However, it is important to note that another important recommendation was discussed in detail in various portions of this report. This recommendation is perhaps the most imporatnt of all. Due to the problems encountered in measuring the concentrations of metal-complexed cyanides, especially $Co(CN)_6^{3-}$, it is highly recommended that another technique be selected and/or developed for QA/QC studies. In this regard, the author of this report believes strongly that, through the vast knowledge that

he gained through the course of this project, he can easily develop a new technique for quatifying their concentrations (Ref. 91). It is recommended that this analysis technique be examined.

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Appendix A

Thermodyanmic Data

GENERAL SPECIES

Water	$-G^o$ (kcal/mole)	Source	Constant (if appropriate)
H^+	0	[Ref. 71]	
OH^-	-37.59	[Ref. 71]	
H_2O (l)	-56.69	[Ref. 71]	

Nitrogen	$-G^o$ (kcal/mole)	Source
CN^-	41.20	[Ref. 71]
HCN (aq)	28.61	[Ref. 71]
OCN^-	-23.28	[Ref. 71]
HOCN (aq)	-27.99	[Ref. 71]
NO_2^-	-7.70	[Ref. 71]
HNO_2 (aq)	-12.09	[Ref. 71]
NO_3^-	-26.59	[Ref. 71]

Carbon	$-G^o$ (kcal/mole)	Source
CO_3^{2-}	-126.15	[Ref. 71]
HCO_3^-	-140.24	[Ref. 71]
H_2CO_3 (aq)	-148.92	[Ref. 71]

COBALT SPECIES

Aqueous	$-G^o$ (kcal/mole)	Source	Constant (if appropriate)
Co^{3+}	32.03	[Ref. 71]	
Co^{2+}	-13.00	[Ref. 71]	
$HCoO_2^-$	-71.58	[Ref. 71]	
$Co(OH)_2$(aq)	-100.79	[Ref. 71]	

Solids	$-G^o$ (kcal/mole)	Source
Co^o	0	[Ref. 71]
$Co(OH)_2$(s)	-109.49	[Ref. 71]

Cyanide Complexes	$-G^o$ (kcal/mole)	Source	
$Co(CN)_3^-$	91.91	[Ref. 76]	$\log(J_3) = 13.7$
$Co(CN)_5^{3-}$	161.62	[Ref. 77]	$\log(J_5) = 23.0$
$HCo(CN)_5^{2-}$	161.84	[Ref. 78]	$\log(K_H) = -0.16$
$HCo(CN)_5^{3-}$	158.09	[Ref. 79]	$\log(K_H) = 2.59$
$Co(CN)_6^{4-}$	208.15	[Ref. 80]	$\log(J_6) = 19.1$

$Co(CN)_6^{3-}$	186.01	[Ref. 81]	$E^o = -0.96$ V with $Co(CN)_6^{4-}$
$Co(CN)_5^{4-}$	185.37	[Ref. 82]	$E^o = -0.96$ V with $Co(CN)_5^{3-}$

GOLD SPECIES

Aqueous	$-G^o$ (kcal/mole)	Source	Constant (if appropriate)
Au^{3+}	103.6	[Ref. 90]	
Au^+	39.0	[Ref. 90]	
AuO_3^{3-}	-5.8	[Ref. 90]	
$HAuO_3^{2-}$	-27.6	[Ref. 90]	
$H_2AuO_3^-$	-45.8	[Ref. 90]	
$Au(OH)_3(aq)$	-61.8	[Ref. 90]	

Solid	$-G^o$ (kcal/mole)	Source
Au^o	0	[Ref. 90]
$Au(OH)_3(s)$	-69.3	[Ref. 90]
AuO_2	-48.0	[Ref. 90]

Cyanide Complexes	$-G^o$ (kcal/mole)	Source
$Au(CN)_2^-$	64.4	[Ref. 90]

ZINC SPECIES

Aqueous	$-G^o$ (kcal/mole)	Source	Constant (if appropriate)
Zn^{2+}	-35.15	[Ref. 71]	
$ZnOH^+$	-78.90	[Ref. 71]	
$Zn(OH)_2(aq)$	-124.94	[Ref. 71]	
$Zn(OH)_3^-$	-165.92	[Ref. 71]	
$Zn(OH)_4^{2-}$	-205.19	[Ref. 71]	

Solid	$-G^o$ (kcal/mole)	Source
Zn^o	0	[Ref. 71]
$Zn(OH)_2(s)$	-132.66	[Ref. 71]

Cyanide Complexes	$-G^o$ (kcal/mole)	Source
$Zn(CN)_4^{2-}$	106.81	[Ref. 71]

IRON SPECIES

Aqueous	$-G^o$ (kcal/mole)	Source	Constant (if appropriate)
Fe^{3+}	-4.27	[Ref. 71]	
$FeOH^{2+}$	-71.58	[Ref. 71]	
$Fe(OH)_2^+$	-108.42	[Ref. 71]	
$Fe(OH)_3(aq)$	-161.90	[Ref. 71]	
$Fe(OH)_4^-$	-201.70	[Ref. 71]	
$Fe_2(OH)_2^{4+}$	-111.68	[Ref. 71]	
Fe^{2+}	-22.05	[Ref. 71]	
$FeOH^+$	-69.54	[Ref. 71]	
$Fe(OH)_2(aq)$	-109.75	[Ref. 71]	
$Fe(OH)_3^-$	-148.48	[Ref. 71]	
$Fe(OH)_4^{2-}$	-185.52	[Ref. 71]	

Solids	$-G^o$ (kcal/mole)	Source
Fe^o	0	[Ref. 71]
$Fe(OH)_2(s)$	-117.84	[Ref. 71]
$Fe(OH)_3(s)$	-170.80	[Ref. 71]

Cyanide Complexes	$-G^o$ (kcal/mole)	Source
$Fe(CN)_6^{3-}$	174.33	[Ref. 71]
$Fe(CN)_6^{4-}$	166.13	[Ref. 71]
$HFe(CN)_6^{3-}$	160.44	[Ref. 71]
$H_2Fe(CN)_6^{2-}$	157.41	[Ref. 71]

Appendix B

QA/QC Data

ACZ

ACZ Laboratories, Inc.
30400 Downhill Drive
Steamboat Springs, CO 80487
(800) 334-5493

Montana Tech of the U. of Montana
1300 W. Park St
Butte, MT 59701
Courtney Young

Client Project ID: PO#10170
ACZ Report ID: RG46248
Date Reported: 6/26/97
Sample Matrix: Miscellaneous

Wet Chemistry		Cyanide, total						M9012 - Automated Colo			
Lab Sample ID Client Sample ID		Sample Date	Receive Date	Result	Qual	Units	MDL	PQL	Date	Analyst
L14051-01	1	6/2/97	6/3/97	116		mg/Kg	5	30	6/25/97	ss/cj
L14051-02	2	6/2/97	6/3/97	108		mg/Kg	5	30	6/25/97	ss/cj
L14051-03	3	6/2/97	6/3/97	124		mg/Kg	5	30	6/25/97	ss/cj
L14051-04	4	6/2/97	6/3/97	117		mg/Kg	5	30	6/25/97	ss/cj
L14051-05	5	6/2/97	6/3/97	165		mg/Kg	5	30	6/25/97	ss/cj
L14051-06	6	6/2/97	6/3/97	182		mg/Kg	5	30	6/25/97	ss/cj
L14051-07	7	6/2/97	6/3/97	144		mg/Kg	5	30	6/25/97	ss/cj
L14051-08	8	6/2/97	6/3/97	69		mg/Kg	5	30	6/25/97	ss/cj
L14051-09	9	6/2/97	6/3/97	44		mg/Kg	5	30	6/25/97	lcj
L14051-10	10	6/2/97	6/3/97	90		mg/Kg	5	30	6/25/97	ss/cj
L14051-11	11	6/2/97	6/3/97	67		mg/Kg	5	30	6/25/97	ss/cj
L14051-12	12	6/2/97	6/3/97	84		mg/Kg	5	30	6/25/97	ss/cj
L14051-13	13	6/2/97	6/3/97	66		mg/Kg	5	30	6/25/97	ss/cj
L14051-14	14	6/2/97	6/3/97	82		mg/Kg	5	30	6/25/97	ss/cj
L14051-15	15	6/2/97	6/3/97	0.07		mg/Kg	0.01	0.05	6/25/97	lcj
L14051-16	16	6/2/97	6/3/97	0.09		mg/Kg	0.01	0.05	6/25/97	lcj
L14051-17	17	6/2/97	6/3/97	52		mg/Kg	5	30	6/25/97	ss/cj
L14051-18	18	6/2/97	6/3/97	67		mg/Kg	5	30	6/25/97	ss/cj
L14051-19	19	6/2/97	6/3/97	52		mg/Kg	5	30	6/25/97	ss/cj
L14051-20	20	6/2/97	6/3/97	0.30		mg/Kg	0.01	0.05	6/25/97	lcj
L14051-21	21	6/2/97	6/3/97	99		mg/Kg	5	30	6/25/97	ss/cj
L14051-22	22	6/2/97	6/3/97	5	B	mg/Kg	1	5	6/25/97	ss/cj
L14051-23	23	6/2/97	6/3/97	4	B	mg/Kg	1	5	6/25/97	ss/cj
L14051-24	24	6/2/97	6/3/97	2.4		mg/Kg	0.2	1	6/25/97	lcj
L14051-25	25	6/2/97	6/3/97	1.7		mg/Kg	0.2	1	6/25/97	lcj
L14051-26	26	6/2/97	6/3/97	4	B	mg/Kg	1	5	6/25/97	ss/cj
L14051-27	27	6/2/97	6/3/97	1.5		mg/Kg	0.2	1	6/25/97	lcj
L14051-28	28	6/2/97	6/3/97	1.8		mg/Kg	0.2	1	6/25/97	lcj
L14051-29	29	6/2/97	6/3/97	98		mg/Kg	5	30	6/25/97	ss/cj
L14051-30	30	6/2/97	6/3/97	110		mg/Kg	5	30	6/25/97	ss/cj
L14051-31	31	6/2/97	6/3/97	123		mg/Kg	5	30	6/25/97	ss/cj
L14051-32	32	6/2/97	6/3/97	141		mg/Kg	5	30	6/25/97	ss/cj
L14051-33	33	6/2/97	6/3/97	137		mg/Kg	5	30	6/25/97	ss/cj
L14051-34	34	6/2/97	6/3/97	124		mg/Kg	5	30	6/25/97	ss/cj
L14051-35	35	6/2/97	6/3/97	129		mg/Kg	5	30	6/25/97	ss/cj

Note: Sample was distilled for Total Cyanide on 6/14/97 within the fourteen day holdtime.

Inorganic Qualifiers (based on EPA CLP-1/90)

U = Analyte was analyzed for but not detected at the indicated MDL.

B = Analyte concentration detected at a value between MDL and PQL

PQL = Practical Quantitation Limit

R V Poulson

Vice President of Operations: Ralph Poulsen

ACZ

ACZ Laboratories, Inc.
30400 Downhill Drive
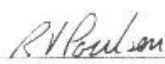Steamboat Springs, CO 80487
(800) 334-5493

Montana Tech of the U. of Montana
1300 W. Park St
Butte, MT 59701
Courtney Young

Client Project ID: *PO#10170*
ACZ Report ID: *RG46249*
Date Reported: *6/26/97*
Sample Matrix: *Miscellaneous*

Wet Chemistry · Lab Filtration · ***

Lab Sample ID	Client Sample ID	Sample Date	Receive Date	Result	Qual	Units	MDL	PQL	Date	Analyst
L14051-03	3	6/2/97	6/3/97						6/12/97	tvw
L14051-04	4	6/2/97	6/3/97						6/12/97	tvw
L14051-07	7	6/2/97	6/3/97						6/12/97	tvw
L14051-10	10	6/2/97	6/3/97						6/12/97	tvw
L14051-11	11	6/2/97	6/3/97						6/12/97	tvw
L14051-14	14	6/2/97	6/3/97						6/12/97	tvw
L14051-17	17	6/2/97	6/3/97						6/12/97	tvw
L14051-18	18	6/2/97	6/3/97						6/12/97	tvw
L14051-21	21	6/2/97	6/3/97						6/12/97	tvw
L14051-24	24	6/2/97	6/3/97						6/12/97	tvw
L14051-25	25	6/2/97	6/3/97						6/12/97	tvw
L14051-28	28	6/2/97	6/3/97						6/12/97	tvw
L14051-31	31	6/2/97	6/3/97						6/12/97	tvw
L14051-32	32	6/2/97	6/3/97						6/12/97	tvw
L14051-35	35	6/2/97	6/3/97						6/12/97	tvw

Inorganic Qualifiers (based on EPA CLP 3/90):

U = Analyte was analyzed for but not detected at the indicated MDL.

B = Analyte concentration detected at a value between MDL and PQL.

PQL = Practical Quantitation Limit

RVPoulsen

Vice President of Operations: Ralph Poulsen

CHAIN OF CUSTODY RECORD

ACZ Laboratories, Inc.
30400 Downhill Drive
Steamboat Springs, CO 80487
(970) 879-8590 • (800) 334-5493

Laboratory Sample Numbers (ACZ Use Only): L14051   COC # 6256

Name to Appear on Report and Invoice:
MT Tech of Montana (Courtney)
1300 W Park St
Attn: Butte MT 59201
Courtney Young   Tel: (406) 496-4158   Attn:

cc: (Report) • (Invoice) to: (circle one or both)

Tel:

REMARKS

See Attached sheets
for sample details
+ analysis requirements

Project or P.O. #
P.O. # 10170

Shipped Via: FED X ___ UPS ___ Hand ___ Other ___

ANALYSES REQUESTED

SAMPLE IDENTIFICATION	DATE	TIME	Sample Matrix *	# of CONTAINERS	Cyanide Total WAD .002% HNO3								
1	6/2/97	9:30	other	3	1								
2	6/2/97	9:30	''	3	1								
3	6/2/97	9:50	''	5	1								
4	6/2/97	9:30	''	5	1								
5	6/2/97	9:30	''	3	1								
6	6/2/97	9:30	''	4	1								
7	6/2/97	9:30	''	5	1								
8	6/2/97	9:30	''	6	1								
9	6/2/97	9:30	''	6	1								
10	6/2/97	9:30	''	5	1								

* Matrix Options: SW (Surface water) • GW (Ground water) • WW (Wastewater) • DW (Drinking water) • SL (Sludge) • SOIL • OIL • Other (Specify)

SAMPLE DISPOSAL OPTIONS - Please complete section A, or choose one option from sections B AND C.
Proper charges will be assessed.

(A) Long-term storage
Hold until _____ (date)
for future analysis.

(B) If Sample is Non-Hazardous
1) Local Disposal
2) RCRA - Permitted Facility
3) Return to Client

(C) If Sample is Hazardous
1) RCRA-Permitted Facility
2) Return to Client

COMMENTS

RELINQUISHED BY: (SIGNATURE)	DATE	TIME	RECEIVED BY: (SIGNATURE)	DATE	TIME	PAGE #
Courtney Young	6/2	9:45		6/3/97	10:20	1
	6/2/97	9.45				OF 4

White - Return w/ sample   Yellow - Return w/ sample   Pink - Return w/ sample   Gold - Keep for your records

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CHAIN OF CUSTODY RECORD

COC # 6256

ACZ Laboratories, Inc.
30400 Downhill Drive
Steamboat Springs, CO 80487
(970) 879-6590 • (800) 334-5493

Laboratory Sample Numbers (ACZ Use Only): L14051

Name to Appear on Report and Invoice:

MT Tech el Mont
1300 W Park St
Butte, MT 59701
Attn: Courtney Young   Tel: (406)866-4154

cc: (Report) - (Invoice) to: (circle one or both)

Attn:
Tel:

Project or P.O. #
P.O. # 10170

Shipped Via: FED X ___ UPS ___ Hand ___ Other ___

ANALYSES REQUESTED

Total Cyanide EPA 4500-CN

SAMPLE IDENTIFICATION	DATE	TIME	Sample Matrix*	# of CONTAINERS	Total Cyanide EPA 4500-CN	
11	6/6/2	9:30	Okw	5	✓	
12	"	"	"	10	/	
13	"	"	"	6	/	
14	"	"	"	6	/	
15	"	"	"	5	/	
16	"	"	"	6	/	
17	"	"	"	5	/	
18	"	"	"	6	/	
19	"	"	"	2	/	
20	"	"	"	5	/	

REMARKS
See attached sheets for sample details + analysis requirements

* Matrix Options: SW (Surface water) - GW (Ground water) - WW (Wastewater) - DW (Drinking water) - SL (Sludge) - SOIL - OIL - Other (Specify)

SAMPLE DISPOSAL OPTIONS – Please complete section A, or choose one option from sections B AND C.
Proper charges will be assessed.

(A) Long-term storage
Hold until _____ (date)
for future analysis.

(B) If Sample is Non-Hazardous
1) Local Disposal
2) RCRA - Permitted Facility
3) Return to Client

(C) If Sample is Hazardous
1) RCRA-Permitted Facility
2) Return to Client

COMMENTS

RELINQUISHED BY: (SIGNATURE)	DATE	TIME	RECEIVED BY: (SIGNATURE)	DATE	TIME	PAGE #
Courtney Young		9:45			6/2	2
Stan McCh		9:45			6/2	OF 4
				6/3/00 10:00		

White - Return w/ sample   Yellow - Return w/ sample   Pink - Return w/ sample   Gold - Keep for your records

CHAIN OF CUSTODY RECORD

ACZ Laboratories, Inc.
30400 Downhill Drive
Steamboat Springs, CO 80487
(970) 879-8590 • (800) 334-5493

Laboratory Sample Numbers (ACZ Use Only): L 14051   COC # 6256

Name to Appear on Report and Invoice:
MT Tech of U of MT
1300 W Park Street
Butte, MT 59701
Attn: Courtney Young   Tel: (406) 496-4158   Attn:

cc: (Report) - (Invoice) to: (circle one or both)

Tel:

Project or P.O. #
P.O. 10170

Shipped Via: FED X ___ UPS ___ Hand ___ Other ___

REMARKS
See attached sheets
for sample details
and analysis requirements

ANALYSES REQUESTED

SAMPLE IDENTIFICATION	DATE	TIME	Sample Matrix*	# of CONTAINERS	Total Cyanide M2-0058-4108							
21	6/2/12	9:30	Other	5								
22	"	"	"	5								
23	"	"	"	5								
24	"	"	"	5								
25	"	"	"	5								
26	"	"	"	6								
27	"	"	"	5								
28	"	"	"	5								
29	"	"	"	5								
30	"	"	"	5								

* Matrix Options: SW (Surface water) • GW (Ground water) • WW (Wastewater) • DW (Drinking water) • SL (Sludge) • SOIL • OIL • Other (Specify)

SAMPLE DISPOSAL OPTIONS - Please complete section A, or choose one option from sections B AND C.
Proper charges will be assessed.

(A) Long-term storage ___ (date)
Hold until ___
for future analysis.

(B) If Sample is Non-Hazardous
1) Local Disposal
2) RCRA - Permitted Facility
3) Return to Client

(C) If Sample is Hazardous
1) RCRA-Permitted Facility
2) Return to Client

COMMENTS

RELINQUISHED BY: (SIGNATURE)	DATE	TIME	RECEIVED BY: (SIGNATURE)	DATE	TIME	PAGE #
Courtney Young	6/2	9:45		6/3/12	1000	3
Steve McAllister	6/2	9:45				OF 4

White - Return w/ sample   Yellow - Return w/ sample   Pink - Return w/ sample   Gold - Keep for your records

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ACZ Laboratories, Inc.
30400 Downhill Drive
Steamboat Springs, CO 80487

SAMPLE RECEIPT FORM

CLIENT: _Mortec_   DATE _6/3/97_

PROJECT #: _L4051_   ANALYST: _BM_

TEMPERATURE VERIFICATION SAMPLE CHECK (°C)

CONTAINER ID	TEMP (°C) 2° to 6°	RAD μR/hr	
Box	15°		If container radioactivity is > 25 μR/hr then each sample must be screened.

PRESERVATION CHECK (pH) & RADIOACTIVITY SCREEN

SAMPLE	R <2	G <2	Y < 2	YG < 2	B < 2	BG < 2	O < 2	T > 12	P > 12	RAD μR/hr

INTERNAL COMMENTS:

REPORT COMMENTS:

Fe (II) Samples

1. Dup. A   UV/H_2O_2 2+ 1 IC
2. Dup. B   UV/H_2O_2 2+ 1 IC
3. Dup. A   UV/TiO_2 4+ 1 IC
4. Dup. B   UV/TiO_2 4+ 1 IC
5. Original (O)   2+ 1 IC
6. Dark (c) - no UV/H_2O_2 3+ 1 IC
7. Dark (c) - no UV/TiO_2 4+ 1 IC

Au (I) Samples

8. Dup. A   UV/H_2O_2 5 + 1 IC
9. Dup. B   UV/H_2O_2 5 + 1 IC
10. Dup. A   UV/TiO_2 4 + 1 IC
11. Dup. B   UV/TiO_2 4 + 1 IC
12. Original (O)   9 + 1 IC
13. Dark (c) - no UV/H_2O_2 5 + 1 IC
14. Dark (c) - no UV/TiO_2 5 + 1 IC

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Zn (II) Samples

15. Dup. A   UV/H_2O_2 4 + 1 IC
16. Dup. B   UV/H_2O_2 4 + 1 IC
17. Dup. A   UV/TiO_2 4 + 1 IC
18. Dup. B   UV/TiO_2 5
19. Original (O)   2 + 1 IC
20. Dark (c) – no UV/H_2O_2 4 + 1 IC
21. Dark (c) – no UV/TiO_2 4 + 1 IC

Co (II) Samples

22. Dup. A   UV/H_2O_2 4 + 1 IC
23. Dup. B   UV/H_2O_2 4 + 1 IC
24. Dup. A   UV/TiO_2 4 + 1 IC
25. Dup. B   UV/TiO_2 4 + 1 IC
26. Original (O)   4 + 2 IC
27. Dark (c) – no UV/H_2O_2 4 + 1 IC
28. Dark (c) – no UV/TiO_2 4 + 1 IC

* This package contains $\underline{\underline{35}}$ samples for Total Cyanide Analysis.

* All samples have been split into $3-10$ aliquots.

* For analysis, the aliquots must be remixed.

* Samples containing TiO_2 will require filtering.

* 10 Samples labeled Dark (c) can not be exposed to UV radiation.

* Sample summary is attached on the next ~~e~~ three pages.

* QA Summary is required because project is EPA - approved / governed.

THANKS!

* All samples were synthetically prepared by

ACZ

ACZ Laboratories, Inc.
30400 Downhill Drive
Steamboat Springs, CO 80487
(800) 334-5493

Montana Tech of the U. of Montana
1300 W. Park St
Butte, MT 59701
Courtney Young

Client Project ID: PO#10170
ACZ Report ID: RG46249
Date Reported: 6/26/97
Sample Matrix: Miscellaneous

Wet Chemistry — Lab Filtration — ***

Lab Sample ID	Client Sample ID	Sample Date	Receive Date	Result	Qual	Units	MDL	PQL	Date	Analyst
L14051-03	3	6/2/97	6/3/97						6/12/97	tvw
L14051-04	4	6/2/97	6/3/97						6/12/97	tvw
L14051-07	7	6/2/97	6/3/97						6/12/97	tvw
L14051-10	10	6/2/97	6/3/97						6/12/97	tvw
L14051-11	11	6/2/97	6/3/97						6/12/97	tvw
L14051-14	14	6/2/97	6/3/97						6/12/97	tvw
L14051-17	17	6/2/97	6/3/97						6/12/97	tvw
L14051-18	18	6/2/97	6/3/97						6/12/97	tvw
L14051-21	21	6/2/97	6/3/97						6/12/97	tvw
L14051-24	24	6/2/97	6/3/97						6/12/97	tvw
L14051-25	25	6/2/97	6/3/97						6/12/97	tvw
L14051-28	28	6/2/97	6/3/97						6/12/97	tvw
L14051-31	31	6/2/97	6/3/97						6/12/97	tvw
L14051-32	32	6/2/97	6/3/97						6/12/97	tvw
L14051-35	35	6/2/97	6/3/97						6/12/97	tvw

Inorganic qualifiers (based on EPA CLP 3290):

U = Analyte was analyzed for but not detected at the indicated MDL

B = Analyte concentration detected at a value between MDL and PQL

PQL = Practical Quantitation Limit

Vice President of Operations: Ralph Poulsen

CHAIN OF CUSTODY RECORD

ACZ Laboratories, Inc.
30400 Downhill Drive
Steamboat Springs, CO 80487
(970) 879-8590 • (800) 334-5493

Laboratory Sample Numbers (ACZ Use Only): L14051 COC # 6256

Name to Appear on Report and Invoice: cc: (Report) - (Invoice) to: (circle one or both)

MT Tech of Environment (Courtney)
1300 W Park St
Butte MT 59201
Attn: Courtney Young   Tel: (406) 496-4158 Attn:

Tel:

Project or P.O. #
P.O. # 10170

Shipped Via: FED X ___ UPS ___ Hand ___ Other ___

REMARKS

See Attached sheets
for sample details
+ analysis requirements

ANALYSES REQUESTED

SAMPLE IDENTIFICATION	DATE	TIME	Sample Matrix*	# of CONTAINERS	Cyanide Total WEeO.CN NJ.OO44					
1	6/2/97	9:30	other	3	1					
2	6/2/97	9:30	''	3	1					
3	6/2/97	9:50	''	5	1					
4	6/2/97	9:30	''	5	1					
5	6/2/97	9:30	''	3	1					
6	6/2/97	9:30	''	4	1					
7	6/2/97	9:30	''	5	1					
8	6/2/97	9:30	''	6	1					
9	6/2/97	9:30	''	6	1					
10	6/2/97	9:30	''	5	1					

* Matrix Options: SW (Surface water) • GW (Ground water) • WW (Wastewater) • DW (Drinking water) • SL (Sludge) • SOIL • OIL • Other (Specify)

SAMPLE DISPOSAL OPTIONS - Please complete section A, or choose one option from sections B AND C.
Proper charges will be assessed.

(A) Long-term storage _____ (date)
Hold until
for future analysis.

(B) If Sample is Non-Hazardous
1) Local Disposal
2) RCRA - Permitted Facility
3) Return to Client

(C) If Sample is Hazardous
1) RCRA-Permitted Facility
2) Return to Client

COMMENTS

RELINQUISHED BY: (SIGNATURE)	DATE	TIME	RECEIVED BY: (SIGNATURE)	DATE	TIME	PAGE #
Courtney Young	6/2	9:45		6/3/97	10:20	1
	6/2/97	9:45				OF 4

White - Return w/ sample   Yellow - Return w/ sample   Pink - Return w/ sample   Gold - Keep for your records

CHAIN OF CUSTODY RECORD

COC # 6256

ACZ Laboratories, Inc.
30400 Downhill Drive
Steamboat Springs, CO 80487
(970) 879-6590 • (800) 334-5493

Laboratory Sample Numbers (ACZ Use Only): L14251

Name to Appear on Report and Invoice:
MT Tech et al at Mont.
1300 W Park SB
Butte, MT 59701
Attn: Courtney Young   Tel: (406) 1856-4158   Attn:

cc: (Report) - (Invoice) to: (circle one or both)

Tel:

Project or P.O. #
P.O. # 10170

Shipped Via: FED X ___ UPS ___ Hand ___ Other ___

ANALYSES REQUESTED

SAMPLE IDENTIFICATION	DATE	TIME	Sample Matrix*	# of CONTAINERS	Total Cyanide EPA 4500-CN					REMARKS
11	6/6/17	9:30	okw	5	✓					See attached sheets for sample details + analysis requirements
12	''	''	''	10	✓					
13	''	''	''	6	✓					
14	''	''	''	6	✓					
15	''	''	''	5	✓					
16	''	''	''	6	✓					
17	''	''	''	5	✓					
18	''	''	''	6	✓					
19	''	''	''	2	✓					
20	''	''	''	5	✓					

* Matrix Options: SW (Surface water) - GW (Ground water) - VW (Wastewater) - DW (Drinking water) - SL (Sludge) - SOIL - OIL - Other (Specify)

SAMPLE DISPOSAL OPTIONS – Please complete section A, or choose one option from sections B AND C.
Proper charges will be assessed.

(A) Long-term storage
Hold until _____ (date)
for future analysis.

(B) If Sample is Non-Hazardous
1) Local Disposal
2) RCRA - Permitted Facility
3) Return to Client

(C) If Sample is Hazardous
1) RCRA-Permitted Facility
2) Return to Client

COMMENTS

RELINQUISHED BY: (SIGNATURE)	DATE	TIME	RECEIVED BY: (SIGNATURE)	DATE	TIME	PAGE #
Courtney Young		9:45	6/2			2
Steve McChe		9:45	6/2		6/8/17 10:00	2 OF 4

White - Return w/ sample   Yellow - Return w/ sample   Pink - Return w/ sample   Gold - Keep for your records

CHAIN OF CUSTODY RECORD

ACZ Laboratories, Inc.
30400 Downhill Drive
Steamboat Springs, CO 80487
(970) 879-6590 • (800) 334-5493

Laboratory Sample Numbers (ACZ Use Only): L 14051   COC # 6256

Name to Appear on Report and Invoice:
MT Tech of U of MT
1300 W Park Street
Butte, MT 59701
Attn: Courtney Young   Tel: (406) 496-4158 Attn:

cc: (Report) - (Invoice) to: (circle one or both)

Tel:

Project or P.O. #
P.O. 1070

Shipped Via: FED X __ UPS ___ Hand ___ Other ___

SAMPLE IDENTIFICATION	DATE	TIME	Sample Matrix*	# of CONTAINERS	ANALYSES REQUESTED			REMARKS
					Total Gravity 50A - 9560-W			See attached sheets for sample details and analysis requirements
21	6/2/02	9:30	other	5				
22	"	"	"	5				
23	"	"	"	5				
24	"	"	"	5				
25	"	"	"	5				
26	"	"	"	6				
27	"	"	"	5				
28	"	"	"	5				
29	"	"	"	5				
30	"	"	"	5				

* Matrix Options: SW (Surface water) • GW (Ground water) • WW (Wastewater) • DW (Drinking water) • SL (Sludge) • SOIL • OIL • Other (Specify)

SAMPLE DISPOSAL OPTIONS - Please complete section A, or choose one option from sections B AND C.
Proper charges will be assessed.

(A) Long-term storage _____ (date)
Hold until _____ for future analysis.

(B) If Sample is Non-Hazardous
1) Local Disposal
2) RCRA - Permitted Facility
3) Return to Client

(C) If Sample is Hazardous
1) RCRA-Permitted Facility
2) Return to Client

COMMENTS

	RELINQUISHED BY: (SIGNATURE)	DATE	TIME	RECEIVED BY: (SIGNATURE)	DATE	TIME	PAGE #
	Courtney Young	6/2	9:45				3
	Steven Gerbler	6/2	9:45		6/3/02	10:00	OF 4

White - Return w/ sample   Yellow - Return w/ sample   Pink - Return w/ sample   Gold - Keep for your records

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Appendix C

QA/QC Summary Report

ACZ Laboratories, Inc.

CASE NARRATIVE
July 17, 1997

Client: Montana Tech
Project: Cyanide Study - PO#10170
Matrix: Synthetic Aqueous
Date Received: 06/03/97
Laboratory Nos.:   L14051-01 through L14051-35

Sample Receipt:

ACZ Laboratories Inc. (ACZ) received thirtyfive aqueous samples from Montan Tech on June 3, 1997. Upon receipt, the sample custodian removed the samples from the cooler, inspected the contents, and logged the samples into ACZ's computerized Laboratory Information Management System (LIMS). The custodian verified the sample information entered into the computer against the chain of custody (COC) forms and sample bottle labels. The samples were actually received in a box at 15 degrees C. No other anomalies were noted regarding the samples receipt.

Holding Times:

All analytes were performed within EPA recommended holding times.

Quality Control:

1.   One duplicate set was flagged on the QC Summary because it was outside the precision acceptance limit of 20%. Several other duplicate sets were within the acceptance criteria. Comparison to historical data and/or data qualification may be necessary. Considering the nature of these samples the problem was probably random and not systematic.

S. Habermehl

Scott Habermehl, Project Management

Appe

ACZ

30400 Downhill Drive
Steamboat Springs, CO 80487
(800) 334-5493
Fax: (970) 879-2216

QC Report ID: QC1339-A

ACZ Project ID: L14051

REPORT TO:

Courtney Young

Montana Tech of the U. of Montana

1300 W. Park St

Butte, MT 59701

7/8/97

Cynthia Clark

Generated by Cynthia Clark, Document Control Assistant

7/8/97

Date

S. Habermehl

Reviewed by Scott Habermehl, Project Manager

7/18/97

Date

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ACZ

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Sample Identification

ACZ Project #	L14051
Client	Montana Tech of the U. of Montana
Client Project ID	PO#10170
Date Received	6/3/97
Date Reported	7/8/97

ACZ Lab ID	Client Sample ID	Sample Matrix	Date Sampled	Date Received
L14051-01	1	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-02	2	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-03	3	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-04	4	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-05	5	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-06	6	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-07	7	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-08	8	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-09	9	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-10	10	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-11	11	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-12	12	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-13	13	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-14	14	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-15	15	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-16	16	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-17	17	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-18	18	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-19	19	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-20	20	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-21	21	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-22	22	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-23	23	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-24	24	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-25	25	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-26	26	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-27	27	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-28	28	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-29	29	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-30	30	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-31	31	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-32	32	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-33	33	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-34	34	Miscellaneous	6/2/97 9:30:00 AM	6/3/97
L14051-35	35	Miscellaneous	6/2/97 9:30:00 AM	6/3/97

Comments:

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Steamboat Springs, CO 80487
(800) 334-5493
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Matrix	Miscellaneous
Analysis Group	Wet Chemistry
QC Report	Calibration Verification-Control Samples

ACZ Project #	L14051
QC Report ID	QC1339-A
Client	Montana Tech of the U. of Montana
Client Project ID	PO#10170
Date Received	6/3/97
Date Reported	7/8/97

Cyanide, total

Method   M9012 - Automated Colorimetric

Associated Client Sxs   L14051-01 to -08, -10 to -14, -17 to -19, -21 to -23, -26, -29 to -35

				Prep Work Group	N/A
				Analytical Work Group	WG42433
				Run ID Number	R32374

ACZ ID	QC Type	PCN / SCN#	Analysis Date	True	Found	Q	Units	Rec (%)	Lower	Upper	Q
WG42433ICV	ICV	PCN5249	6/25/97 12:06:00 AM	0.3	0.32		mg/L	106.7	90	110	
WG42433CCV1	CCV	PCN5249	6/25/97 12:18:00 AM	0.2	0.197		mg/L	98.5	90	110	
WG42433CCV2	CCV	PCN5249	6/25/97 12:30:00 AM	0.2	0.193		mg/L	96.5	90	110	
WG42433CCV3	CCV	PCN5249	6/25/97 12:42:00 AM	0.2	0.1994		mg/L	99.7	90	110	
WG42433CCV4	CCV	PCN5249	6/25/97 12:54:00 AM	0.2	0.2		mg/L	100	90	110	
WG42433CCV5	CCV	PCN5249	6/25/97 12:59:00 AM	0.2	0.198		mg/L	99	90	110	

Method   M9012 - Automated Colorimetric

Associated Client Sxs   L14051-09, -15 to -16, -20, -24 to -25, -27 to -28

				Prep Work Group	N/A
				Analytical Work Group	WG43122
				Run ID Number	R32404

ACZ ID	QC Type	PCN / SCN#	Analysis Date	True	Found	Q	Units	Rec (%)	Lower	Upper	Q
WG43122ICV	ICV	PCN5249	6/25/97 12:06:00 AM	0.3	0.323		mg/L	107.7	90	110	
WG43122CCV1	CCV	PCN5249	6/25/97 12:18:00 AM	0.2	0.199		mg/L	99.5	90	110	

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		Matrix	Miscellaneous
		Analysis Group	Wet Chemistry
		QC Report	Calibration Verification-Blanks

ACZ Project #	L14051
QC Report ID	QC1339-A
Client	Montana Tech of the U. of Montana
Client Project ID	PO#10170
Date Received	6/3/97
Date Reported	7/8/97

Cyanide, total

Method   M9012 - Automated Colorimetric

Associated Client Sxs   L14051-01 to -08, -10 to -14, -17 to -19, -21 to -23, -26, -29 to -35

		Prep Work Group	N/A
		Analytical Work Group	WG42433
		Run ID Number	R32374

ACZ ID	QC Type	Analysis Date	Concentration			Control Limits		Units	Q
			MDL	Found	Q	Lower	Upper		
WG42433ICB	ICB	6/25/97 12:07:00 AM	0.01	0.006		-0.01	0.01	mg/L	
WG42433CCB1	CCB	6/25/97 12:19:00 AM	0.01	0.005		-0.01	0.01	mg/L	
WG42433CCB2	CCB	6/25/97 12:31:00 AM	0.01	0.004		-0.01	0.01	mg/L	
WG42433CCB3	CCB	6/25/97 12:43:00 AM	0.01	0.007		-0.01	0.01	mg/L	
WG42433CCB4	CCB	6/25/97 12:55:00 AM	0.01	0.006		-0.01	0.01	mg/L	
WG42433CCB5	CCB	6/25/97 1:00:00 AM	0.01	0.005		-0.01	0.01	mg/L	

Method   M9012 - Automated Colorimetric

Associated Client Sxs   L14051-09, -15 to -16, -20, -24 to -25, -27 to -28

		Prep Work Group	N/A
		Analytical Work Group	WG43122
		Run ID Number	R32404

ACZ ID	QC Type	Analysis Date	Concentration			Control Limits		Units	Q
			MDL	Found	Q	Lower	Upper		
WG43122ICB	ICB	6/25/97 12:07:00 AM	0.01	0.006		-0.01	0.01	mg/L	
WG43122CCB1	CCB	6/25/97 12:19:00 AM	0.01	0.005		-0.01	0.01	mg/L	

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Matrix	Miscellaneous
Analysis Group	Wet Chemistry
QC Report	Spike Verification

ACZ Project #	L14051
QC Report ID	QC1339-A
Client	Montana Tech of the U. of Montana
Client Project ID	PO#10170
Date Received	6/3/97
Date Reported	7/8/97

Cyanide, total

Method   M9012 - Automated Colorimetric

Associated Client Sxs   L14051-01 to -08, -10 to -14, -17 to -19, -21 to -23, -26, -29 to -35

Prep Work Group	N/A
Analytical Work Group	WG42433
Run ID Number	R32374

ACZ ID	QC Type	PCN / SCN#	Analysis Date	Added	Sample	Q	Spike	Q	Units	Rec (%)	Lower	Upper	Q
L14051-08AS	AS	WC970217-1	6/25/97 12:17:00 AM	0.1	0.0462		0.1382		mg/L	92	75	125	
L14051-12AS	AS	WC970217-1	6/25/97 12:35:00 AM	0.1	0.168		0.2665		mg/L	98.5	75	125	
L14051-35AS	AS	WC970217-1	6/25/97 12:58:00 AM	0.1	0.258		0.358		mg/L	100	75	125	

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ACZ

30400 Downhill Drive
Steamboat Springs, CO 80487
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Fax: (970) 879-2216

Matrix	Miscellaneous
Analysis Group	Wet Chemistry
QC Report	Duplicate Verification

ACZ Project #	L14051
QC Report ID	QC1339-A
Client	Montana Tech of the U. of Montana
Client Project ID	PO#10170
Date Received	6/3/97
Date Reported	7/8/97

Cyanide, total

Method   M9012 - Automated Colorimetric

Associated Client Sxs   L14051-01 to -08, -10 to -14, -17 to -19, -21 to -23, -26, -29 to -35

									Prep Work Group	N/A
									Analytical Work Group	WG42433
									Run ID Number	R32374

ACZ ID	QC Type	Analysis Date	Concentration				Units	RPD (%)	Control Limits (%)		Q
			Sample	Q	Duplicate	Q			Lower	Upper	
L14051-12DUP	DUP	6/25/97 12:34:00 AM	84		82		mg/L	2.4	0	20	
L14051-26DUP	DUP	6/25/97 12:48:00 AM	4	B	4.53	B	mg/L	12.4	0	20	
L14051-34DUP	DUP	6/25/97 12:57:00 AM	124		126.1		mg/L	1.7	0	20	

Method   M9012 - Automated Colorimetric

Associated Client Sxs   L14051-09, -15 to -16, -20, -24 to -25, -27 to -28

									Prep Work Group	N/A
									Analytical Work Group	WG43122
									Run ID Number	R32404

ACZ ID	QC Type	Analysis Date	Concentration				Units	RPD (%)	Control Limits (%)		Q
			Sample	Q	Duplicate	Q			Lower	Upper	
L14057-09DUP	DUP	6/25/97 1:09:00 AM	44.51		59		mg/L	28	0	20	X

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Steamboat Springs, CO 80487
(800) 334-5493
Fax: (970) 879-2216

Matrix	Miscellaneous
Analysis Group	Wet Chemistry
QC Report	Method Verification-Control Samples

ACZ Project #	L14051
QC Report ID	QC1339-A
Client	Montana Tech of the U. of Montana
Client Project ID	PO#10170
Date Received	6/3/97
Date Reported	7/8/97

Cyanide, total

Method   M9012 - Automated Colorimetric

Associated Client Sxs   L14051-01 to -08, -10 to -14, -17 to -19, -21 to -23, -26, -29 to -35

Prep Work Group	N/A
Analytical Work Group	WG42433
Run ID Number	R32374

ACZID	QC Type	PCN / SCN#	Analysis Date	Concentration True	Found	Q	Units	Rec (%)	Control Limits,% Lower	Upper	Q
WG42433LCSW	LCSW	WC970620-1	6/25/97 1:02:00 AM	0.2	0.194		mg/L	97	80	120	
WG42433LCSW1	LCSW	WC970620-1	6/25/97 1:04:00 AM	0.2	0.2		mg/L	100	80	120	

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	Matrix	Miscellaneous
	Analysis Group	Wet Chemistry
	QC Report	Method Verification-Blanks

ACZ Project #	L14051
QC Report ID	QC1339-A
Client	Montana Tech of the U. of Montana
Client Project ID	PO#10170
Date Received	6/3/97
Date Reported	7/8/97

Cyanide, total

Method   M9012 - Automated Colorimetric

Associated Client Sxs   L14051-01 to -08, -10 to -14, -17 to -19, -21 to -23, -26, -29 to -35

Prep Work Group	N/A
Analytical Work Group	WG42433
Run ID Number	R32374

ACZID	QC Type	Analysis Date	Concentration				Control Limits		Q
			MDL	Found	Q	Units	Lower	Upper	
WG42433PBW	PBW	6/25/97 1:01:00 AM	0.01	0.007		mg/L	-0.02	0.02	
WG42433PBW1	PBW	6/25/97 1:03:00 AM	0.01	0.005		mg/L	-0.02	0.02	

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Appendix D

Ion Chromatography Data

Table D.1 % Remediation of UV-Irradiated Metal-Complexed Cyanide Test Solutions Based on Nitrite and Nitrate Concentrations Determined by Ion Chromatography

Sample No.	Metal Complex	Photolytic Reagent	Initial CN^- (ppm)	NO_3^- Conc. (ppm)		NO_2^- Conc. (ppm)		EquivalentC N^- Conc. (ppm)		% Remediation	
1	$Zn(CN)_4^{2-}$	H_2O_2	62.4	143	138	2.5	6.4	61.5	61.6	98.6	98.7
2	$Fe(CN)_6^{4-}$	H_2O_2	148	55	51	8.8	7.6	28.1	25.7	19	17.4
3	$Au(CN)_2^-$	H_2O_2	78	34	87	15	5.3	22.8	39.6	29.2	50.8
4	$Fe(CN)_6^{3-}$	H_2O_2	156	99	107	19	22	52.3	57.4	33.5	36.8
5	$Co(CN)_6^{3-}$	H_2O_2	156	9	5.7	9	4.2	8.87	4.77	5.7	3.1
6	$Zn(CN)_4^{2-}$	TiO_2	62.4	2.3	3.9	0.9	1.7	1.47	2.6	2.4	4.2
7	$Fe(CN)_6^{4-}$	TiO_2	148	27	21	8.2	5.1	16	11.7	10.8	7.9
8	$Au(CN)_2^-$	TiO_2	78	27	17	5.1	3.4	14.2	9.1	18.2	11.7
9	$Fe(CN)_6^{3-}$	TiO_2	156	75	51	3.3	4.9	33.4	24.2	21.4	15.5
10	$Co(CN)_6^{3-}$	TiO_2	156	34	27	1.1	2.6	14.9	12.8	9.6	8.2

Table D.2 % Remediation of Non-Irradiated Metal-Complexed Cyanide Test Solutions Based on Nitrite and Nitrate Concentrations Determined by Ion Chromatography

Sample No.	Metal Complex	Photolytic Reagent	Initial CN^- (ppm)	NO_3^- Conc. (ppm)	NO_2^- Conc. (ppm)	EquivalentC N^- Conc. (ppm)	% Remediation
11	$Zn(CN)_4^{2-}$	H_2O_2	62.4	129	14	62.1	99.5
12	$Fe(CN)_6^{4-}$	H_2O_2	148	21	12	15.6	10.6
13	$Au(CN)_2^-$	H_2O_2	78	16	17	16.3	20.9
14	$Fe(CN)_6^{3-}$	H_2O_2	156	54	22	35.1	22.5
15	$Co(CN)_6^{3-}$	H_2O_2	156	1.2	5.6	3.67	2.4
16	$Zn(CN)_4^{2-}$	TiO_2	62.4	0.8	0.5	0.62	0.99

17	$Fe(CN)_6^{4-}$	TiO_2	148	0.6	0.5	0.53	0.36
18	$Au(CN)_2^-$	TiO_2	78	1.1	0.3	0.63	0.81
19	$Fe(CN)_6^{3-}$	TiO_2	156	1.2	0.4	0.73	0.47
20	$Co(CN)_6^{3-}$	TiO_2	156	1.7	0.5	0.99	0.64